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CONDUCTED BY

LORD KELVIN, LL.D. P.R.S. &c.

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AND

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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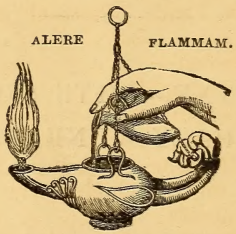
"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.



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[FIFTH SERIES.]

JANUARY 1893.

I. *The Electrical Properties of Pure Substances.*—Part I. *The Preparation of Pure Nitrogen and attempts to Condense it.* *By* Professor R. THRELFALL*.

[Plate I.]

IN 1886 a paper was published in the Proceedings of the Royal Society by Professor J. J. Thomson and myself, "On an Effect produced by the passage of an Electric Discharge through Pure Nitrogen." The effect in question was briefly as follows:—When a nitrogen tube provided with a small mercury or sulphuric-acid gauge is exhausted to a pressure of about 8 millim. of mercury and then sparked with a discharge too small to heat the tube in a sensible manner, a diminution of the elastic force of the enclosed gas is observed. This diminution was found to be independent of the size or material of the electrodes, of the volume of the tube or the extent of its surface, but to depend on the kind of discharge employed, and its duration; on the temperature and pressure of the gas in the tube during the process of sparking and afterwards. Arguing by exclusion, we attributed the diminution of pressure to a condensation of nitrogen molecules, similar to the condensation which oxygen undergoes when converted into ozone.

This property of nitrogen, if established, would be of undoubted interest, and consequently in 1889 I undertook a

* Communicated by the Author.

repetition of the experiments with a view to testing our conclusions by an extended examination of the phenomena in question. This investigation has proved a most laborious task; and it was not until December 1891 that I finally satisfied myself that the effect was due to the combination of nitrogen with the mercury of the pressure-gauge under the influence of the electric discharge, and in the presence, as I think, of a minute trace of some other substance whose nature I have not been able to determine.

The experiments to be described leave little doubt that pure nitrogen at ordinary temperatures does not condense in the same way that oxygen condenses, whether the discharge be by means of external electrodes or by means of wires fused into the tube. Since these experiments form the starting-point of other researches, I will begin by an account of a method by which pure nitrogen may be most advantageously prepared. Singularly enough this apparently simple chemical problem has not, so far as I know, been solved hitherto. Stas, in his researches, makes the remark that nitrogen is easily obtained pure (*Bulletin de l'Académie Royale des Sciences de Belgique*, 1860, sér. 2, t. x. p. 254); and this remark may very possibly have produced misunderstanding—everything depends on what is meant by the word pure. The fundamental principles in all processes of purification are:—1st, that reagents used to remove any impurity must really keep the impurity when they have got it, and not liberate it or its equivalent through any instability of the compounds formed; and 2nd, that the reagents themselves must not give rise to impurities. As an example of a common violation of the first principle, I will mention the absorption of sulphuretted hydrogen, sulphur dioxide, or the oxides of nitrogen, by potash or soda; and of the second, the use of imperfectly prepared phosphorus pentoxide. Trouble arising from layers of air or other gases condensed on the surfaces of glass vessels can only be relieved by arranging the method of production of the gas required in such a way that the glass surfaces may remain for weeks or months in contact with the gas under experiment, otherwise completely purified. If mercury be in contact with glass in any part of the apparatus, then, as I believe, it is impossible by ordinary means to be sure that the glass is ever completely denuded of its primitive layers of gas. I append a list of some of the various ways in which nitrogen has been prepared for careful work, and shall, I think, be able to show that all these processes are open to objection, at all events where a continuous supply of gas is necessary. The list is short, because nearly all experimenters simply state that

they used pure nitrogen without giving details of its method of preparation.

Name.	*Reference.*	*Method.*
J. S. Stas	*Bull de l'Acad. de Belgique*, vol. x. p. 254.	By passing purified air over hot copper turnings and gauze, which are previously reduced by hydrogen. Copper oxide at end of tube (?); ordinary absorbent reagents to help purify the gas after leaving the hot copper.
Neuman	*J. für prk. Chemie*, [2] xxxvii. p. 342.	From chloride-of-lime cubes (made by Winkler's method) and aqueous ammonia (see C. S. J. 1887, p. 442).
Olzewski	*Wien. Anzeiger*, March 1884.	Hot copper and air.
Wroblewski ..	*C. R.* xcviii. p. 982.	Hot copper and air.
Lupton	C. S. J. 1876; Chem. News, xxxiii. p. 90.	Air and ammonia over hot copper; claims to get pure N with a short tube.
H. Deslandres.	*C.R.* ci. p. 1256.	Hot copper and air; no precaution mentioned.
W. Gibbs....	*Ber.* x. p. 1387.	Sodium nitrite, ammonium sulphate, and potassium dichromate in excess. If there is a trace of chloride present, impurities are introduced.
N. W. Fisher.	Pogg. *Ann.* xvii. p. 137.	Uses cuprous chloride as an absorber of oxygen from air.
Regnault	*C. R.* t. xx. p. 975.	Hot copper and air.
Wüllner	Pogg. *Ann.* cxlvii. p. 325.	Burning phosphorus in air over mercury and removing traces of oxygen by incandescent iron wire.
Huggins	Phil. Trans. 1860.	Purified air over hot reduced copper.
Warburg	*Ann. der Chem. und der Phys.* 1887, p. 548.	Hittorf's method. Dust-free air over hot white phosphorus, then over potassium permanganate, solid potash, and phosphorus pentoxide. Special drying in some cases followed by exposure (Wied. *Ann.* xl. p. 1) to nascent sodium obtained by the electrolysis of glass.

It is clear that the most popular way of making nitrogen is to absorb the oxygen from air by means of red-hot copper. There are a great many objections to this method, however, even when precautions are taken against the possibility of the formation of oxides of nitrogen. In the first place, a satisfactory method of making connexion to the porcelain tube is unknown to me; indiarubber stoppers are undesirable in any

case, and particularly in places where they can become hot. One never feels certain, moreover, that a red-hot tube, even of glazed porcelain, is absolutely impermeable to furnace-gases. If one uses a bath of magnesia this difficulty may perhaps be overcome, but there remains the difficulty of making proper connexions.

If hard glass be employed instead of porcelain, then there is insecurity in the joints between it and the glass used for the remainder of the apparatus. Metal tubes present similar difficulties with regard to the junctions, and are besides more or less porous at high temperatures. Another grave disadvantage is that, whether porcelain or glass tubes be used, there is always a chance of a crack occurring, and perhaps escaping notice.

The reduction of the copper also presents great difficulty: it is more difficult to get a strong stream of really pure hydrogen or carbon monoxide than to get the nitrogen; and any sulphur absorbed by the copper is a permanent disadvantage; for, as metallurgists know, copper containing sulphur may be oxidized and reduced many times and yet at each oxidation some sulphur will burn out. The reason is, of course, that sulphide of copper heated in air forms some sulphate of copper as well as sulphur dioxide. On the next reduction sulphide of copper is re-formed, and then, on passing air over the mixture, the process of incomplete oxidation is repeated. Judging by a discussion which took place in Section A of the British Association not long ago, these simple facts are not as widely known as might have been expected. I know of no reagent which will absorb sulphur dioxide so as to form an absolutely stable compound, and which is itself easy to prepare in a state of sufficient purity to be above suspicion of giving off foreign matters to the nitrogen. Of course it may be argued that a large number of vessels containing, say, a solution of caustic potash might be used, the second retaining the sulphur dioxide given off from the first, and so on; but this device is obviously unsuited for a continuous process, where the reagents must be untouched for weeks or months.

Finally, I gave the process a careful trial, and found it unsatisfactory from the causes mentioned; and, as a matter of fact, the trouble of preparing hydrogen or carbon monoxide in a sufficient state of purity to reduce the copper without contaminating it with sulphur or chlorine is at least as great as the trouble of preparing nitrogen itself.

With regard to the method of passing air over melted white phosphorus, the manipulation of phosphorus is always

troublesome, and I have not been able to find any information as to whether phosphorus absorbs gases which might be given off during the process of the removal of oxygen from air. Warburg used a solution of potassium permanganate to absorb the vapour of phosphorus; but I have not been able to obtain information as to whether such a solution is to be relied on, in the first place to remove all the phosphorus, and in the second to give off nothing else during the process. I understand, from the paper in Wied. *Ann.* vol. xl. 1890, p. 1, that Warburg, in his later experiments, did not succeed to his satisfaction in removing the last trace of oxygen by this method, but had to electrolyse the glass of his vacuum-tubes so as to liberate the sodium in presence of the nitrogen, in order to get rid of the last traces of oxygen and hydrogen. This method appears satisfactory if one has at one's disposal a sufficient electromotive force, suitable glass, and an infinite time: the hydrogen appears to be absorbed as by palladium.

Another method over which I spent six months of fruitless labour is based on the decomposition of ammonium bichromate by heat. This method is convenient, because if the bichromate could be got to deliver nitrogen of suitable quality, small quantities of the salt could be decomposed in bulbs fused on to the vacuum-tubes along with suitable purifying reagents. Ordinary ammonium bichromate (*i. e.* that sold as pure) gives off a good deal of ammonia and oxides of nitrogen as well as nitrogen itself and water-vapour. This means the use of a good many purifying reagents, so that the method loses its advantages of simplicity; and in addition the oxides of nitrogen cannot be fixed satisfactorily by any suitable reagent known to me. I thought, however, that possibly very pure ammonium bichromate might decompose in a simpler manner, and consequently went to great trouble to procure a pure sample. For this purpose I purified a large quantity of ammonium chloride and sulphate by the method described by Stas (*Bull. de l'Académie Royale de Belgique*, 2nd sér. t. x. p. 283), repeating the boiling with nitric acid more often than Stas found requisite. The purified samples were used to generate gaseous ammonia (under the influence of specially prepared marble-lime), which after copious washing was absorbed by chromic acid. Some samples of this ammonia were passed over red-hot platinized asbestos with sufficient pure oxygen* to destroy three quarters of the ammonia, $4NH_3 + 3O_2 = 6H_2O + 2N_2$, with a view to destroying any traces of organic ammonium compounds; but the

* The method of procuring pure oxygen will be described in another connexion.

resulting bichromate of ammonium coming from the small quantity of ammonia which was not destroyed by the oxygen did not differ in behaviour from the other samples. It may be noted here that Stas found (*loc. cit.*) that purified ammonia has a much less unpleasant smell than ordinary ammonia: careful trial, however, failed to enable me to detect any difference between the smell of my purest ammonia and that obtained by boiling so-called pure solution of ammonia obtained from the dealers. I conclude that the "pure ammonia" of commerce is much purer now-a-days than it was thirty years ago.

The chromic acid was made from repeatedly crystallized bichromate of potash, bought as pure, and the sulphuric acid which is sold for analytical purposes. The resulting chromic acid was washed free from sulphuric acid by strong nitric acid, distilled for the purpose. I found incidentally that the addition of a little chromic acid to the mixture of nitric and sulphuric acid in the retort appeared to have a good effect in diminishing the quantity of nitrous acid which generally accompanies "fuming" nitric acid. The washed chromic acid was dried on tiles in the usual way, and heated with great care and continual stirring until it partly melted; but even so it was slightly decomposed. Of course the greater portion of the nitric acid had been previously got rid of by heating the chromic acid on a water-bath in a partly exhausted retort with ground-on condenser, the latter containing some sticks of potash. The chromic acid being partially decomposed gave a solution, which had to be filtered through glass-wool before it was used to absorb the ammonia. This solution was tested by distilling, the distillate being tested for nitrites both before and after reduction with sodium amalgam. The result of these tests was to show that either the solution contained no nitro-compounds, or, if so, not more than are contained in the same quantity of platinum distilled water. The bichromate of ammonia made from this was recrystallized three times from platinum distilled water. Some small samples were crystallized up to six times, but did not differ from the results of the third crystallization. All these samples, when heated either in air or *in vacuo*, gave off nitrous compounds, and did not behave in any way differently to the sample which had been bought as pure. I therefore conclude that the normal decomposition of ammonium bichromate is complex, and that it is not a good substance to use as a source of nitrogen.

I will now describe a method of procuring nitrogen which has not been mentioned hitherto, which lends itself remarkably well to a continuous process, and which is almost, but not

quite, free from objection. I refer to the copper-ammonia and chromous-chloride method of Berthelot and Recoura ('Watts' Dictionary,' new edition, and *Ann. de Phys. et de Chim.* s. 6, vol. x. p. 5). When air is exposed to a large surface of copper wet with strong ammonia, the oxygen is for the most part absorbed. In my experience with the arrangements about to be described, there is only about three per cent. of oxygen left after the reagents have acted for half an hour, and only one per cent. after three hours. Since in practice with my apparatus the air often stands over the copper for a day or even a week, the absorption is probably nearly complete. The last traces of oxygen are absorbed by a strong solution of chromous chloride, which perhaps exercises a stronger absorptive power on oxygen than any other liquid, and is for this purpose quite easily prepared. As the method is not so well known as it deserves to be, I give the following description from Recoura's paper:—

A large flask is taken, and in it are placed 250 to 300 grammes of granulated redistilled zinc with 50 grammes powdered crystals of potassium bichromate. The bichromate must be finely powdered; it should be pounded till it looks bright yellow. Three hundred cubic centimetres of pure hydrochloric acid are mixed in a beaker with two hundred cubic centim. of water, and I have found it advantageous to heat the mixture almost to boiling. The contents of the beaker are then poured as quickly as possible into the flask, and a violent evolution of hydrogen and steam at once commences. If the flask is too small, some of the liquid will of course be projected from it. Under the powerfully reducing influence of the zinc and hydrochloric acid, the chromium is rapidly reduced to the state of green oxide, which then redissolves to a beautiful blue solution. The whole reaction only takes about ten minutes or a quarter of an hour. If the bichromate is not sufficiently finely powdered, a further quantity of hydrochloric acid may have to be added to complete the reaction, or the mixture may be left (excluding air) for a few hours. The blue solution contains chromous chloride, chlorides of zinc and potassium, and possibly various impurities. The slightest trace of oxygen destroys the perfect colour of the chromous chloride by converting it into the green or grey substances investigated by Recoura. On standing over zinc for some time, however, if not too much oxidized and slightly acid, the chromium compounds become again reduced and the fine blue colour reappears. The colour is as clear and bright and almost exactly of the same shade as the colour of an ammoniacal solution of cupric hydrate. Recoura states that a stream of gas containing free oxygen

can be completely deprived of the latter by allowing it to bubble once through a flask containing the blue liquid. To test this I placed two flasks in series, both containing a few hundred centimetres of the solution, and fitted with tubes allowing air to be sucked through both, one after the other. Though I allowed the air to pass much more briskly than if I had been actually using the process (say three times faster than one ordinarily allows the oxygen to pass in an organic analysis), I did not observe any change in the second flask till the first had long been quite opaque and had become more than warm, and then suddenly the contents of the second flask became attacked. In manipulating the chromous-chloride solution, it is useful to have a flask of the blue liquid permanently at hand to purify the carbonic acid or nitrogen which must be used in the subsequent operations. In many cases it does not matter whether the gas has a trace of hydrogen in it or not; but for my purpose I was not willing to run any risk of having hydrogen about, and consequently I never allowed the purifying flask to contain zinc.

Having satisfied myself as to the reliability of the chromous chloride as an absorber of oxygen, I undertook a number of experiments with the object of discovering, 1st, the most suitable form in which to use it; 2nd, whether in the process of absorption any other gas was given off, or any vapour which could not be safely absorbed. In these experiments large vessels containing copper and ammonia (arranged in a manner to be presently explained), and capable of furnishing a continuous steam of nitrogen mixed with oxygen in proportions which could be varied at will, were used throughout. The ammonia was removed from the nitrogen by strong sulphuric acid that had been heated to boiling and cooled in a vacuous desiccator. With regard to the best way of using the chromous chloride, I began with the impression that tubes filled with the dry salt would be the most convenient, especially as Recoura shows that small crystals of dry chromous chloride have an affinity for oxygen which surpasses that of the solution. I therefore prepared large quantities of the blue solution, and obtained the crystals from it by the method recommended by Recoura, which is briefly as follows:—The blue liquid is mixed with a saturated solution of sodium acetate, which precipitates chromous acetate in the form of a dark red powder. This powder is then dissolved in dilute hydrochloric acid, and the chromous chloride precipitated from the solution by passing in gaseous hydrochloric acid so as to gradually increase the strength of the hydrochloric-acid solution

The crystals are repeatedly washed with strong hydrochloric acid and dried by pressing them into tubes with Kieselguhr. All these operations require to be performed in an atmosphere free from oxygen, and consequently are troublesome. The crystals are of a fine sky-blue colour, and have a really extraordinary affinity for oxygen. For my purpose, however, I disliked the use of the sodium acetate, because I never felt quite sure that I had washed all the resulting acetic acid out of the crystals. I have no reason to believe that, even if acetic acid were present during the absorption of oxygen, any organic compound would be liberated, but in the absence of any information I thought it better not to run the risk. I therefore turned my attention to the original blue solution. This of course contains chlorides of zinc and potassium, free hydrochloric acid, hydrogen in solution, and possibly traces of sulphur compounds coming from impurity in the potassium dichromate. It is a question, then, whether during the absorption of oxygen we may not have chlorine or sulphur compounds liberated. Both the acid and zinc were free from arsenic and antimony, so that I had no uneasiness about these substances. I first satisfied myself that chlorine was not given off, by allowing nitrogen with 3 per cent. of oxygen to pass through two flasks of chromous chloride, and then through copper sulphate to retain traces of hydrochloric acid, and finally over paper dipped in a solution of iodide of potassium and starch. Though ten litres of gas were passed through, I could detect no change in the starch-paper. Sulphuric acid, when added to the blue liquid, is partly reduced and hydrogen sulphide is given off; consequently, since potassium bichromate is generally contaminated with potassium sulphate, which is hard to remove, I had to test whether any sulphur compounds were evolved. For this purpose, and with the arrangement of the last experiment, I passed nitrogen through the liquid and then over filter-paper, saturated with a slightly acid solution of nitrate of silver, but no change of colour could be detected. It remained for me to make sure that in the liquid I intended to use there could be no volatile impurity (the traces of hydrochloric acid itself need not be considered, because hydrochloric acid can be stopped readily by potassium hydrate).

Before discussing this I must explain my method of preparing the blue liquid, which was as follows :—About ten litres of the raw product were prepared in several operations and drawn into one large vessel through a filtering-tube. This tube contained a length of four inches of compressed glass-wool, and was closed at its lower end by a perforated platinum

plate whose edges were fused into the tube. The blue liquid was forced through the plug by a pressure of carbonic acid made from marble, which had been boiled for a good many hours at reduced pressure in water before being placed in the Kipp's apparatus. This carbonic acid always passed through a wash-bottle of blue litmus purified in the way to be described by a preliminary experiment. The filter acted so perfectly that the liquid passing through it was brilliantly clear and free from zinc-dust, which I greatly feared. In these preliminary operations I was practically forced to make use of some rubber-stoppers, and this is the worst fault of the method. However, all the stoppers used were well coated with pure paraffin; and though they might have given off some hydrocarbons, still I was unable to detect any trace of them in the nitrogen finally obtained. Some rubber-tubing was also employed to make joints, but the same precautions were taken with it, and in all cases the sulphur was well cleaned off. The filtered liquid was finally got into a retort with a ground-on condenser, and was concentrated to one third of its original volume in a brisk current of carbonic acid.

Towards the end of the operation the stream of carbonic acid was stopped, and a partial vacuum was created in the retort and condenser by a water-pump, so that the final concentration took place under reduced pressure. These precautions were considered sufficient to remove the hydrogen dissolved in the liquid as well as any traces of volatile sulphur compounds resulting from supposed impurities in the potassium bichromate. The resulting liquid was a clear blue syrup, and was transferred at once to the absorption-apparatus. Before going into any details as to other precautions, I will describe the arrangements adopted for the continuous preparation of the nitrogen by this process. These arrangements will be most easily understood by a reference to the diagram (Pl. I.), though taps and clips are exaggerated for clearness. *g* is a pipe projecting through the window of the laboratory, and terminating close to the wall at a height of about three metres from the ground. The University paddock separates the laboratory by nearly a quarter of a mile from the nearest road on this side, but the road on the other side lies within 150 yards. The elevation of the laboratory is 120 feet above sea-level. Consequently the composition of the air is probably more nearly that of typical "country air" than of town air. H is a U-tube with paraffin (M.P. 51° C.) covered cork stoppers, and is tightly packed with cotton-wool, from which the dust was blown before the tube was mounted. F is a two-way tap,

enabling the large glass vessel to be placed in communication either with the external air through H, or with the system of purifying tubes. The large vessel with tap E is filled with copper gauze and strip, and communicates by a tube having a rubber-joint and clip D and tap C with another large vessel placed 2·4 metres above it (measured from bottom to bottom). The upper vessel can be put in communication with a water-pump by a pipe passing through B and having a tap at A. This upper vessel contains strong liquid ammonia. It will be readily understood that by working the taps &c. the ammonia may be drawn into the upper vessel while air is being admitted to the lower, and may then be allowed to descend by gravity, and furnish the requisite head to force the gas through the remainder of the apparatus when the two-way tap F is suitably turned. G is an auxiliary tap for allowing samples of the gas to be drawn off and tested for oxygen in an ordinary Hempel's gas-analysis apparatus, not shown in the diagram. The air, from which the greater part of the oxygen has been absorbed by the copper and ammonia, now passes into a horizontal tube I about half filled with strong sulphuric acid, where the greater portion of the ammonia is absorbed. The management of this tube requires care or the entrance soon gets stopped up by the formation of ammonium sulphate. After two years' work this tube was replaced by a large glass wash-bottle with ground-in stopper. J is a tube containing strong sulphuric acid through which the gas bubbles; *h* is merely a drawn-out end for facilitating the blowing-out of the joints of the glass tubes. At K are two "double" wash-bottles containing the chromous chloride syrup; and L represents a U-tube with ground-in tap-stoppers filled with glass beads, and likewise containing chromous chloride. The stoppers of L and K are weighted with lead weights to enable them to stand the pressure, and mercury cups are arranged round the stoppers. M is a tube containing a solution of caustic potash. N contains nitrate of silver together with a little silver hydroxide and potassium nitrate, O contains more potash, and P contains strong sulphuric acid. Q is half filled with potash in lumps, and half with soda-lime. R is a tube into which phosphorus pentoxide has been distilled so as to present a large surface. S, a Winchester bottle with ground-in stopper, and the wide tube U both contain phosphorus pentoxide. Originally there was a mercury-gauge at V, and though this was dispensed with, the apparatus for eliminating mercury vapour was allowed to remain because one or two drops of mercury had got into the tube near V. W is a specially fine tap protected with

mercury; and X is a little phosphorus-pentoxide tube required to protect the tap, which is lubricated with phosphorus pentoxide, and which of course requires to be kept at the proper degree of concentration. Y is a sulphur tube, and at Z are silver and copper tubes. Beyond Z is seen a tube and gauge of the type used in experimenting on the nitrogen at low temperatures. Σ is a small phosphoric-acid guard-tube, Ψ is a sulphur tube, and Ω and Φ are silver and copper tubes separated from each other by long tubes of capillary bore. This system divides at *b*, so that it may be put in communication with a water-pump *viâ d*, *a*, and *e*, or a Geissler pump through *f*, where there is another tap not shown. The taps at F, W, *d*, and *f* are fine samples of the diagonal taps made by the successors of Geissler, of Bonn; they have all been reground with "optical" precision, and are all lubricated (except F) with phosphorus pentoxide and protected with mercury. The weak point in the system is at the stoppers of L and K, which had to be lubricated with tallow. In order to satisfy myself of the nature of the tallow I began by purifying it with animal charcoal, and finally by keeping it melted for eight hours in a vacuum. After this the smell was almost gone and the tallow was applied to the stoppers mentioned. The tap F was lubricated with vaseline and beeswax also long melted *in vacuo*. I feared that I should introduce hydrocarbons at these points, but the convenience of using the tallow caused me to try it, and undertake an examination of the gas in a vacuum-tube in order to find whether any hydrocarbons were present or not. The result was that no trace of the "three" bands could be found, so that the enormous complications which would have been required in the other event were happily unnecessary. The stoppers of the large ammonia vessels were of paraffin-coated rubber. It will be noticed that all the points where tallow or rubber were used are to the right of the main purifying system, which includes strong sulphuric acid, and the grinding of all the stoppers was so accurate that an almost inappreciable film of tallow was all that was necessary. It remains to describe the precautions taken with the various reagents, beginning on the right.

Ammonia.—The examination of the ammonia sold as "pure liquid ammonia" which I made in connexion with the ammonium bichromate experiments showed that nothing was to be gained for the purpose of the main experiment by attempting any further purification.

Copper.—At different times sheet gauze, wire, and turnings were employed. The purity of the copper does not

seem to be of importance, but it is necessary to get rid of grease. This must be done in such a way as not to waste too much copper. In order to clean the turnings and gauze they were soldered into a copper tube, and a considerable quantity of shale benzine was distilled and allowed to condense among them. This secures that every part shall be wetted. The process was then continued by gasoline. The gasoline was distilled over the copper to avoid residues, and was finally dried out at about 120° for twelve hours, a good stream of filtered air being drawn over the copper by means of an air-pump. The same process was gone through with alcohol, and finally water. The copper was then washed with dilute chromic acid and digested with strong ammonia for half an hour. All this trouble was gone to, to avoid wasting the turnings, which one has to cut oneself in order to get them in nice long curls, so that they will stand in the bottle and not break up at once and go to the bottom. After about a year's work it was found necessary to renew the copper and ammonia—the former having almost disappeared in a yellow red mud (cuprous oxide ?) which was not further examined—and the ammonia solution had also partially lost its blue colour. Copper strip about 1 millim. thick was now used to replace the gauze and turnings and wire, and was of course strong enough to stand dipping in nitric and sulphuric acid. It is, on the whole, more convenient to use copper in strip than any other form.

Sulphuric Acid.—This was bought as pure for analysis, and was heated with pure ammonium sulphate for some time before being used. Its purity was, however, of no great moment, except in the case of the final drying-tube P.

Chromous Chloride.—Already discussed.

Potassium Hydrate.—During the experiments on the decomposition of ammonium bichromate, I incidentally noticed that all the samples of potash and soda in my possession yielded traces of nitrites, either on simple solution or when distilled with strong sulphuric acid (which was itself free from this impurity) and the distillate reduced by sodium amalgam. The samples of potash which were said to have been purified by solution in alcohol were the worst in this respect, while some rough lumps of commercial caustic potash were nearly free from the impurity in question. I found considerable quantities of nitrites also in samples of potash procured by exposing clean potassium to moist air. I did not try with dry air. After a good deal of trouble I was reduced to using a solution of a sample of potash in sticks not specially purified, but which only gave the reaction very

slightly, and was boiled under diminished pressure for two or three hours before use. The solution still gave a distillate with sulphuric acid which reacted with starch and iodine, but after a time so long that it was possible that the exposure to air during the experiment had been sufficient to supply the nitrite discovered. In fact a control experiment made with some ammonia, known to be free from nitrites or nitrates, yielded a distillate which coloured to nearly the same extent on standing. The solution was made up to the strength recommended for use in organic analysis.

Silver Nitrate.—Crystals of silver nitrate bought as pure were dissolved in platinum distilled water to make a ten-per-cent. solution ; to this, when in the tube, a little of the potash solution was added—so as to form a little silver hydroxide. This hydroxide darkened gradually in the bright light to which it was exposed. It was not considered necessary to investigate the solution for traces of free nitrous compounds, as the gas on leaving it passed through another potash-tube.

Solid Potash and Potash-Lime.—The above-mentioned stick potash was used, and the potash-lime was made by adding a little of the solution to some marble-lime prepared in the laboratory ; the drying process was carried out in a clean iron dish.

Phosphorus Pentoxide.—This, being the last reagent traversed by the nitrogen, requires to be exceptionally carefully treated. I began by acting on a hint obtained in 1889 from Prof. Josiah P. Cook, of Harvard, and endeavoured to prepare a pure sample of the pentoxide by burning phosphorus in a very strong draught of air, rather than by attempting to purify the ordinary commercial reagent. For this purpose an elaborate sheet-iron cylindrical chamber, measuring 3 feet by 2 feet, was prepared and fitted with suitable contrivances for carrying out the combustion of several pounds of phosphorus. The air-blast was obtained from a Root's blower worked by a gas-engine, and the filtered air travelled through a tin tube about 4 feet long and 7 inches in diameter, filled with calcium chloride in the state usually described as "rough dried." After many attempts a large quantity of excellent pentoxide was obtained, which, however, though indefinitely better than the commercial product, still retained traces of phosphorus. The tests I employed for the purpose of discovering whether the pentoxide contained free phosphorus or not were the following:—(1) Dissolving 10 or 15 grammes weight of the pentoxide in clear distilled water and observing (α) whether anything remains undissolved, (β) whether, at the moment of throwing the phosphorus pentoxide on the

water any smell of phosphorus can be detected. (β) is a good deal more delicate than (α), for I clearly discerned the smell of phosphorus after the pentoxide had become pure enough to yield no perceptible particles when thrown into water. (2) A small porcelain crucible was filled with the pentoxide to be tested, the lid was replaced, and the crucible rapidly raised to a dull red heat, or till the pentoxide just began to distil off. The room in which the operation was conducted was quite dark except for the fickle light emitted by the Bunsen flame used in heating the crucible. As soon as the proper moment arrived the observer adjusted the crucible tongs with one hand and turned out the Bunsen with the other. The cover of the crucible was then removed, and by turning on a tap ready to hand a jet of oxygen was caused to impinge on the phosphorus pentoxide in the crucible: if any phosphorus is present "sparkles" are seen on the surface of the pentoxide; and if the room is dark and the eyes of the observer sensitive this is a very good test, but not quite so good as that by the smell caused by throwing a large quantity of the pentoxide on water. (3) A few drops of a solution of chloride of gold in ether were mixed with about 500 cub. centim. of water, so as to make a very dilute solution. This solution was divided into two parts and occupied two similar cylinders. To one portion the solution obtained by throwing about 1 gramme of the pentoxide into 100 cub. centim. of water was added, and to the other an equal quantity of pure water. The observation, lasting for several days, consisted in watching the cylinders and noting the reduction of gold that took place, as evidenced by the rosy purple colour which the solution assumed. This test is not so delicate as the others, and is valueless unless a control experiment is made in the manner here described.

As tested by these tests, the phosphorus pentoxide prepared by myself was never quite free from phosphorus, and I was therefore obliged to undertake the distillation of the raw product in a stream of oxygen. This of course involved the making of the oxygen in a sufficient state of purity. Fortunately the presence of nitrogen in oxygen used for this purpose is of no consequence so long as the amount is not large, the impurities to be dreaded are hydrocarbons and chlorine. The oxygen was consequently prepared from potassium chlorate with the usual precautions as for an organic analysis, being passed through several potash-tubes and wash-bottles on its way to the gas-holder—a large copper one free from grease on the taps. From the gas-holder the oxygen passed through the following system:—

(1) Solution of potassium hydrate in tube 4 feet long.

*(2) Tube 18 in. long, first half filled with metallic antimony, second half filled with clean silver foil.

(3) U-tube 12 × 1 in., solution of silver nitrate.

(4) U-tube 12 × 1 in., solid potash.

(5) 2 ditto, sulphuric-acid beads.

(6) 1 bottle, phosphorus pentoxide.

(7) 2 U-tubes, ditto.

All the connexions were of glass throughout, but it was found convenient to use several rubber stoppers coated with hard paraffin. The distillation of the pentoxide was carried on in a porcelain tube 2 centimetres in diameter and nearly a metre long, the connexions being made with glass tubes pushed into the ends of the porcelain tube, and packed with glass-wool and some pentoxide. This packing is very firm and good. The first three quarters of the porcelain tube were nearly filled with pentoxide, the last quarter contained platinized porcelain and asbestos, the latter most carefully purified by boiling in hydrochloric acid and strong heating. The distillation was carried on in some cases so as to cause the pentoxide to condense in the tubes and vessels in which it was to be used, and a considerable quantity was also collected in a bottle.

The final product passed all the tests I have enumerated, and was used throughout the nitrogen apparatus, even for drying the pump, lubricating the taps, &c. Of course a good many tubes full of pentoxide were distilled, and nearly three months were consumed in obtaining the final product. If I had not had the assistance of Mr. J. A. Pollock in this work, I have an impression that I might be at it still. The commercial pentoxide was used in this work, for the substance we prepared ourselves was probably good enough for most purposes as it was. I have sometimes wondered whether experimenters who have of late used so much pentoxide for critical work on gases have recognized the necessity of testing the product obtained by distilling the pentoxide in oxygen. In my experience, unless the oxygen stream be very strong it is quite possible to fail to remove the last traces of free phosphorus.

Sulphur†.—I happened to have some very pure sulphur which had been prepared for another purpose. It will be

* It was found as the result of several preliminary experiments that metallic antimony is a rather good absorber of chlorine, and keeps what it absorbs.

† An account of the experiments with sulphur will form a chapter of this monograph.

sufficient here to say that the sulphur was originally precipitated from calcium polysulphides by hydrochloric acid; it was laboriously ground and washed, and distilled five times, and care was taken not to let it take fire. The degree of purity attained was tested by burning off large quantities in a burnished platinum dish, and continuing the process till the residue had disappeared. This product was rather precious, consequently it was made the most of in the present case by using it to coat glass beads; some in powder was also employed near the entrance of the purifying tubes.

Copper and Silver.—Both bought as pure and deprived of grease by dipping in appropriate acid solutions.

General Remarks.—During the two years the apparatus has been in use various accidents, such as the breaking of pumps &c., have at different times caused some of the reagents to get mixed up, and the apparatus has been taken down and set up again some three or four times; the first bottles of chromous chloride have also required to be refilled. The phosphorus pentoxide has never required to be touched. I wish to draw attention to a remark of Hittorf's as to the importance of using tubing free from air-bubbles. On several occasions I have been much troubled by the minute leaks which such imperfect tubes give rise to at the joints, and I have in my possession at least two tubes leaking from this cause, but so minutely that even when the leak was localized to within six or seven inches it was impossible to say exactly where it was. In work of this kind the cleaning of the tubes is of course of great importance. If the work is to be done rapidly the great secret is to clean the tube with alcohol before the jointing or general glass-blowing operations are carried out on it. The dirty places are almost always near where the blowpipe-flame has been applied, and after trying all and every means of cleaning, I have finally come back to *aqua regia* caused to boil at the dirty place and left in the tube for at least ten hours. Certainty of cleaning and jointing has led me to employ English flint glass exclusively in this work, and I always use the clean flame of an oxygen-gas blowpipe, which saves time so as to far more than repay the cost of the oxygen. All the blowing required in jointing the tubes is done through a compact but efficient establishment of filtering and phosphoric-acid tubes. The glass springs so extensively used throughout allow of considerable latitude in the relative movements of parts of the apparatus, and I have had no cases of spontaneous breaking. The whole of the glass work has been done by myself, as I can get no assistance of a suitable kind in Sydney.

It may possibly be objected that some of the precautions taken are finnicking, and that (as in the manufacture of the oxygen) an unnecessary variety of absorptive materials are used. The reply I should make to such a criticism is that the complete operation of any one reagent is always to some small extent hypothetical, and I consider that by varying the reagents one helps to get rid of the chance of the persistence of impurities so small in amount as to be beyond the range of ordinary analysis, *i. e.* beyond the point up to which we are certain of the action of the reagents.

Testing the Gas for Hydrocarbons and Hydrogen.

In order to avoid the impurities introduced by the presence of internal electrodes, a tube was prepared with external electrodes. It was about 35 centim. long, of which length 20 centim. were made of capillary tube. In order to fill this with the pure gas, the apparatus was exhausted three times, as far as the chromous chloride U-tube, each exhaustion requiring seven or eight hours' work with the Geissler pump, after a good water-pump had got rid of the greater part of the gas.

The pressure of the remaining gas was imperceptible by inspection of the pump-gauge (of which a description will be given), but the pump continued on each occasion to show a just appreciable bubble of gas when the mercury flowed into the barometer-tube. The pumping was done at times separated from each other by three or four days in order to give the residual gas from the walls of the vessel time to come off; of course this gas was removed as it appeared. The pressure I should judge was, on each occasion, about of the order of ·01 millim. Several bottles of gas were also forced through the apparatus at the ordinary pressure.

Finally, on Feb. 19, 1891, the tube together with another for experimental purposes were fused off—the former at about ·1 millim. pressure (the latter will be dealt with later). The tube had previously been heated till the glass began to soften and the walls to fall in, and the gas admitted had been for several days in contact with the phosphorus pentoxide. The only objection to the external electrode tube is that I have hitherto failed to produce a line-discharge in it—though of course Prof. J. J. Thomson's method (Phil. Mag. vol. xxxii. 1891) would give it in an endless tube without electrodes, and if the method had been known at the time I should have employed it. However, I got a bright bluish-white discharge in the narrow tube (the larger ends being golden), and this

yielded a fine band-spectrum which has been described often enough, showing well both in the more and less refrangible ends. I took as my authority on the typical hydrocarbon bands those mentioned in the B.A. Report for 1880, p. 226.

Observer.	Wave-length.
Ångström and Thalén . .	5633 at least refrangible end.
Watts	5634·7
Ångström and Thalén . .	5164
Watts	5165
Ångström and Thalén . .	4736
Watts	4739

Professors Liveing and Dewar (Proc. Roy. Soc. vol. xxx.) say that the characteristic spectrum of hydrocarbons is composed (among others) of four bands in the orange, yellow, green, and olive. These were well seen by me in an olefiant-gas tube prepared for the purpose without any pretensions to purity. The cone of a Bunsen flame was also examined, and I saw the lines (according to my map)

α	at	5637	instead of	5634	
β	„	5164	„	5165	(strongest)
γ	„	4736	„	4738	

I had a number of commercial tubes and examined these as a check; the following is the result:—

β turned up in petroleum and alcohol but not in olefiant gas, where there was a band at 5197 to 5198. This last band was strong and was seen in CO_2, H, O, turpentine, petroleum, and coal-gas, as well as in the olefiant gas. I do not know what this band is due to, but it did not appear in the nitrogen. The nitrogen was examined side by side with an alcohol tube showing α and β well; but the former did not show these bands or any trace of them. The nearest band was at 5240, and quite too far away for there to be any mistake. The experiment was also tried with a similar tube and nitrogen at 10 millim. pressure, with a like result. Finally the examination was repeated at the lowest pressure at which I could get a brilliant discharge, which was of course far beyond the limit of discrimination of my pressure-gauge. The result was the same as before. The red and blue hydrogen lines were never seen in any of my tubes showing banded spectra. This analysis is of course dependent partly on the accuracy of our map, though when once the typical lines were picked up, their coincidence or not could be determined by direct expe-

riment. It was necessary, therefore, to make a map of the spectrum to suit my spectroscope. The latter was an instrument with a 5-in. Trouton and Sims circle, and was made by Elliott Bros.; one fine heavy glass prism was used throughout, and the map refers to it; it was always in the position of minimum deviation for each line observed. The mapping of the spectrum was done for me by Mr. J. H. D. Brearley (a student in the laboratory), who also assisted at this time in all the spectroscopic work and to whom my thanks are due. The map was made by a selection of 33 lines drawn from all sorts of sources, and verified in all sorts of ways, the tables used being those in the B.A. Reports for 1884, 1885, 1886; Rowland's map (got in 1889); and Rowland's table, Phil. Mag. 1889. Schellen was also found of some use. Each line was set upon ten times; and the prism was adjusted ten times.

Intermediate lines were now well picked up off Rowland's map. Our limit of discrimination was about 2 in the fourth significant figure of the wave-length, *i. e.* I could not decide with certainty that a line I made out to be at, say, 5165 was not at 5163.

I append a list of the lines used in mapping the spectrum, not because it is in any way to be regarded as a model selection, but because I, as a beginner at spectroscopy, should have been very glad of such a list at the time, had I been able to find one. I also note the means adopted by us for the identification of the lines, as it may interest other beginners in spectroscopy. The lines are not given in the order in which they were examined, but in order of wave-length.

1.—B. Sun, 6867·796–6867·462. Rowland, Phil. Mag. June, 1889. Recognized by being near both to a large iron and to a potassium line.

2.—Li_α, 6705·4. From lithium chloride in a Bunsen flame. Wave-length from B.A. Report, 1884; given by Mascart, Liveing and Dewar, and Thalén.

3.—C. Sun (hydrogen). Good line recognized by comparison with a tube-spectrum of H_2O. $\lambda = 6563·042$. Rowland, Phil. Mag. 1889.

4.—Sun, 6400·2. A good line picked up when the map was nearly finished from Rowland's map.

5.—Sun, 6191·7. Same as number 4.

6.—Li_β, 6102. Authority, Mascart.

7.—Iron line, 5930·4. Rowland's map verified by comparison with spark-spectrum of iron. B.A. Report. Cornu gives 5929·3.

8.—D. Halfway between the two lines. Mean, $\lambda=5893$. Rowland, Phil. Mag. 1889. Compared with sodium flame.

9.—Picked up from Chart. $\lambda=5709{\cdot}8$.

10.—Barium (γ). From flame-spectrum of Ba $(NO_3)_2$. B.A. Report, 1884. Liveing and Dewar. $\lambda=5534{\cdot}3$. A bright line.

11.—Magnesium, $\lambda=5528$. Rowland's map and spark-spectrum.

12.—Thallium (α), $\lambda=5349$. B.A. Report, 1885. Liveing and Dewar, and de Boisbaudran. Got from flame-spectrum.

13.—Iron, 5328·2. Rowland's map verified by spark-spectrum. A good line.

14.—E. $\lambda=5270$. Rowland's map, a big double. Picked up at first because it was found from Schellen's map that it was between two cobalt lines and near an iron line. These lines were seen in their proper relative places in the spark-discharge from iron and cobalt. This was one of the first lines identified.

15.—b_1, 5183·798. Rowland, Phil. Mag. Verified by magnesium-spectrum. One of the first lines got.

16.—$\lambda=5041$–5042. Picked up from Rowland's map. Verified by finding from B.A. Report that it was an iron line and then confirming by spark-spectrum.

17.—$\lambda=4957{\cdot}6$. Picked up and verified as in the last case.

18.—$\lambda=4920{\cdot}6$. Ditto.

19.—F. $\lambda=4861{\cdot}492$–$4859{\cdot}929$. Rowland's map confirmed by vacuum-tube.

20.—Bismuth. $\lambda=4752$. B.A. Report, Thalén, and Huggins. From spark-spectrum. Not very good. Evidence as to identification, its general relation and appearance.

21.—Bismuth. $\lambda=4724{\cdot}5$. A very prominent line. Evidence and authority as in last case.

22.—Bismuth. $\lambda=4705$. Ditto. These lines cannot be mistaken.

23.—Strontium blue line. $\lambda=4607$. From flame-spectrum. B.A. Report, 1884. Liveing and Dewar, Thalén, Huggins.

24.—Cæsium β. $\lambda=4597$. B.A. Report, 1884; de Boisbaudran and Lockyer (4592). de Boisbaudran's value was taken, rather to my regret. One of the first lines got. Flame-spectrum.

25.—Cæsium α. $\lambda=4555$. Liveing and Dewar; B.A. Report, 1884; Lockyer and de Boisbaudran (4560). Flame-spectrum.

26.—Indium blue line. $\lambda=4509{\cdot}6$. Liveing and Dewar and Thalén, B.A. Report, 1884. Took Liveing and Dewar's number. Flame-spectrum.

27.—Solar spectrum. $\lambda=4405$. Rowland's map. Schellen's map gives it identical with an iron line. Verified by spark.

28.—Solar spectrum. $\lambda=4383{\cdot}6$. As in case of last line (27).

29.—Solar spectrum. Hydrogen violet. $\lambda=4340{\cdot}5$. Rowland's map and vacuum-tube.

30.—Solar spectrum. $\lambda=4325{\cdot}982$. A fine line. Rowland's map and Phil. Mag. 1889. Picked up from map.

31.—Solar spectrum G. $\lambda=4308{\cdot}023$. Rowland's map and Phil. Mag. The subject of a misprint in Rowland's list in Phil. Mag. 1889. It is an iron line.

32.—Solar spectrum. $\lambda=4227$. A calcium line given in Schellen's map. Well seen on Rowland's map. Could not verify from flame.

It will be found that the lines mentioned in this list are well spaced, and a curve drawn to them will enable most of the other lines to be set upon by calculation. It is obvious that all sorts of appliances must be to hand in order to verify the lines in the first instance, as well as a good stock of the rarer metals and their salts.

Preparation of Pump-Gauge.—All gauges of closed U-type. Gauge 1 constructed of tube 3 centim. in diameter, and 3 millim. thick in the walls, tested for evenness, &c. Each limb about 20 centim. long, one limb closed at the top and the other open to the pump. The bend constructed of thick tubing having a bore of rather less than 1 millimetre in diameter. This gauge was boiled out in a good Sprengel vacuum some twenty times, but I never could get rid of the last minute traces of gas. I have an idea that the last trace of gas cannot be got rid of—it can only be reduced asymptotically. However, the gauge was excellent; it was painted black, except for a slit down each limb, and was read (with the precautions mentioned by Regnault) by one of the Cambridge Scientific Instrument Company's (Poynting's) cathetometers from about three metres' distance. This gauge behaved admirably, and I used it during the spectroscopic work; in some of the preliminary tube-experiments at a low pressure, however, a joint broke, and the momentum of the mercury was sufficient to break the closed end of the gauge in spite of the constricted bend. Under the circumstances, the gauge being much better than was required, I made No. 2

similar to it, but of only 1 centim. diameter, and having a finer constriction of thermometer-tube in the bent part. This tube was not so good as the last, as it was not gas-free, and a small correction amounting to half a millimetre or so had usually to be applied on this account. This correction was determined several times, and a table of readings and corrections made out. There is no uncertainty as to the readings beyond about ·05 millim., a quantity wholly insignificant for our purpose. This gauge lasted till 1892, when I finally got tired of applying corrections, and made a new and better gauge on the same lines and of the same dimensions. This is still in use.

Tube Pressure-Gauge.—A glance at the Plate will show that this gauge was similar to the one used by Professor Thomson and myself in 1885, with the exception that it was of glass throughout. A tube of about 2 centim. diameter is bent into a U-shape, the bend being of tube about ·5 millim. in diameter. The limbs are about 5 centim. long. The mercury is introduced so as to stand about halfway up the wide tubes. The upper ends of the limbs are connected to each other, so that the gauge is really a "ring" space, and the space above the mercury communicates with the experimental tube by a filamentary glass tube of from one to two metres in length. When it is desired to observe the change of pressure in the spark-tube, the connexion between the space over the free surface of the mercury in the two limbs is interrupted by fusing a previously narrowed neck into a solid mass. This of course allows the pressure in the closed limb to retain its initial value, whatever that may be; while the pressure in the open limb varies with the pressure in the tube.

The effect of the metre-long filamentary tube is to hinder the diffusion of mercury vapour into the sparking-tube; and this in one or two experiments was also attended to by including a tube filled with clean silver foil between the mercury and filamentary tube. The filamentary tube, however, never let enough mercury-vapour in to give a mercury-spectrum at the lowest pressure at which I worked. Of course the mercury in the gauge was carefully boiled several times in order to cause any considerable quantity of gas that might have been condensed to be given off before the experiment began. These gauges, of which large numbers were made at one time and another, were very satisfactory, and when observed with proper precautions by means of the cathetometer, would certainly betray a difference of pressure of about ·05 millim., all sources of uncertainty being taken into account.

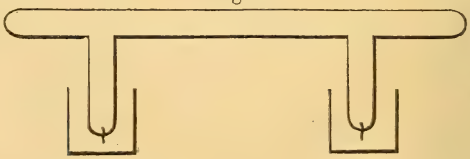
Experimental Spark-Tube.—The first successful tube was furnished with external electrodes and sparked between Feb. 24 and March 2, 1891. Details are (pressure 8·8 millim.) :—

		h	m	
Feb. 24.	Sparked	1	30	Sparks being long and thin, large resistance in circuit.
Feb. 25.	„	5	0	Ditto.
Feb. 28.	„	3	0	Ditto. Then 3 hours 15 minutes with less resistance.
Mar. 2.	„	4	0	The least perceptible discharge.

No effect was noticed at any time. The tube was left for three days in order that the temperature might reach the exact value it had when the gauge was sealed, and it happened that this did not occur for three days. There was still no effect. This tube was sealed from the pump in series with the spectrum-tube and is still in my possession.

Tube 2.—After experimenting with many tubes mostly of the form shown in the diagram (fig. 1), with the armed ends in mercury cups, a satisfactory tube was got on April 21st.

Fig. 1.



The difficulty arose from my determination to have the electrodes white hot for several hours by a preliminary sparking at about ·1 millim. before the tube was finally filled with gas and sealed off. The excessive heating of the electrodes generally broke the glass. During this time I noticed a thing which was new to me, but which I daresay is well known, viz., the ease with which the colour of the fluted spectrum-discharge may be made to change. Thus on the 20th I found that at a pressure of less than 1 millim., and with a very intense discharge from a coil giving 12-in. sparks without condenser, I could cause the golden-coloured discharge to become pinkish by heating the tube with a bare flame to about 200° C., a necessary step in the preparation. The spectrum, of course, merely showed a shift in relative luminosity from the red towards the blue end. The action was reversed on cooling the tube. This could be repeated once or twice. However, with the next filling of gas the experiment did not succeed at all, no heating of the tube caused any change in the colour of

the discharge; and in subsequent experiments only variable results were met with. The tube in question was finally sealed off at 9·2 millim., and sparked for six hours without effect. The next day the sparks were made stronger, and sent through the tube for four hours; still no effect was produced. The tube then cracked on the next attempt to spark it.

Tube 3.—April 25. Pressure 9·4 millim. In preparing the tube I noticed what I always noticed afterwards, viz., that at about 2–3 millim. the discharge begins by being pink, and then in a minute or two becomes golden, and keeps so. On turning off the spark and reducing the pressure to about 1 millim., the same effect is observed. I have noticed this effect in all the tubes prepared since my attention was first directed to it. The sparking of this tube was as follows:—

April 25. 4 hours with the effective sparks described in the former paper. No effect.
April 27. 6 hours ditto. No effect.
April 28. 4 hours. Sparks of various intensity. No effect.
April 29. 4 hours. Ditto. Ditto.

This tube was sound throughout, and the result was convincing. It then occurred to me that possibly the mercury used in our gauges might account for the results obtained by Professor Thomson and myself in 1886. At that time we used a gauge fused directly on to the discharge-tube, with perhaps 10 centim. of 2-millim. tubing between the mercury surface and the tube, and with globules of condensed mercury hanging to the walls of the connecting-tube almost up to the discharge-tube itself. I remember that the glow often extended down to the mercury.

Tube 4.—Made with a side tube containing some very pure and dry mercury, so as to imitate our older form of tube. Pressure 8·5 millim.

June 11. Sparked 3 hours with effective sparks. No effect.

June 12. Sparked 4 hours with effective sparks. Examined on 15th, when it showed a just perceptible diminution of pressure.

June 15. Sparked 8 hours. Effect increased to about 1·2 millim. In order to try whether large sparks would reduce the effect, as was formerly found to be the case, I increased the intensity of the discharge, but did not succeed in producing any increase of pressure during half an hour (except that due to rise of temperature). The tube was then carefully examined, and it was found by holding a sheet of white paper

behind it that there was a slight appearance of a bronze-coloured fog in the tube near the mercury-pocket.

June 16. A strong discharge sent through the tube so that it became warm to the hand, say 40° C.; the discharge was kept on for three hours.

June 18. The temperature again being the same as when the tube was sealed, it was noted that the effect appeared to have increased by about ·2 millim. in spite of the strong discharge. Two "gallon" Leyden jars were then included in the circuit provided with an air-gap, and parallel to the spark-tube. During two hours' sparking the effect went on increasing, and the bronze-coloured stain on the glass grew deeper near the drops of mercury till it became a black mirror.

This was of course partly due to the volatilization of the mercury near the drops. The effect had increased to about 7 millim. by the next morning, when the temperatures had become uniform.

June 19. Sparked, say, 5 hours. Effect on cooling was now 7·3 millim., indicating that only about 1·2 millim. of gas was left in the tube.

June 20. The mirror of mercury compound, which had now become very black about the narrow tube and in the part of the spark-tube near it, was heated with the Bunsen flame. After some heating, say at about 250° C., the film began to crepitate audibly and emit flashes and sparks of blue flame. The deposit turned brownish as the temperature rose, the sides became indistinct, and finally the flash and crackling noise came on and the film vanished, leaving a clear bright tube. The process was repeated till the mirror of mercury had been chased all over the tube; and even then the gauge only came back far enough to show a pressure-difference of 4·2 millim. in the same direction as before—*i. e.* it only came back by 3·1 millim. The ends of the tube, where the the electrodes were fused in, were not heated; and this may have accounted for the persistency of the diminution of pressure. In order to test this the tube was removed from the mercury cups and placed in an extemporized air-bath made out of a kerosene tin. Several thermometers were ranged alongside the tube, and the whole apparatus was covered by an asbestos cloth. The bath was heated by a Bunsen burner. A good many rather elaborate readings of temperature and pressure were taken on June 20, the temperature rising to about 170° C. in the middle of the tube and to a few degrees less at the ends. These readings turned out to have no significance, in consequence of a doubt

as to whether the ends of the limbs of the tube into which the wires were fused were or were not at the same temperature as the rest of the tube. However, there is no doubt that the temperature of the ends was over 150° C., and yet when all was cold again it was observed that the effect still amounted to a difference of pressure of 3·4 millim.

Now a compound of mercury and nitrogen, described as trimercuramine, was obtained by Plantamour (*Ann. Chem. Pharm.* xl. p. 115) by passing ammonia gas over mercuric oxide. This substance is said to explode on heating, and Plantamour gave it the formula Hg_3N_2 on the strength of its behaviour with copper oxide in a combustion-tube, though he did not analyse it. The formula is, however, probably not very far from being correct. Plantamour does not state the temperature at which the nitride explodes, but says that if a little heap of the substance be placed on a card or piece of paper, and heated over the flame of a spirit-lamp, the explosion will occur before the temperature is high enough for the paper to be turned yellow. My compound certainly required a higher temperature than this to start the explosion; but it is possible that its being in a nearly vacuous space, and very much contaminated with free mercury, may have had something to do with this. Plantamour's compound exploded with a white flame, which was bluish red at the edges; the compound I obtained emitted a brilliant bluish-white light on explosion. There is some evidence from Plantamour's paper that a temperature exceeding 200° C. prevents the formation of the nitride from mercuric oxide and ammonia gas, and that the best temperature at which to carry out the synthesis is 150° C. These facts appear to point to the conclusion that mercury nitride is a dissociable compound; and the substance I obtained is probably so, as the continuation of the history of the tube will show. On June 22 the tube was wrapped in a good deal of copper gauze, and the bundle so made and into which three thermometers passed was placed in the air-bath. The burners were regulated so as to give a stationary temperature, first of 185° C. and then of 196° C. At the former temperature the gauge appeared to show that some substance was still undecomposed; but there is some uncertainty, from the ratio of the volume of the spark-tube to the gauge-tube not being exactly known. Estimating these volume-ratios, however, as nearly as possible by means of external measurement, and applying the necessary corrections, I found that the pressure ought to be (as shown by the gauge) 5 millim. greater on the tube side than on the sealed side. The observed pressure-difference was 5·2 millim.—a better agreement

than one had any right to expect. The temperature was kept constant for a quarter of an hour after the observation, in the hope of detecting any further change, should it take place; but the readings remained constant. I am therefore inclined to the belief that the substance dissociates on heating, and is all decomposed at a temperature of about 190° C. On June 23rd, when all parts of the apparatus were again at a uniform temperature, the original effect had almost returned, there now being a difference of pressure of 3·2 millim. between the tube and the sealed space; or, in other words, partial recombination of the nitrogen appeared to have taken place.

Other matters required my attention at this time, and I did not get an opportunity to continue the study of the tube till August 13. On this day the pressure-difference was 3·7 millim., apparently showing that slow recombination had been going on. On August 13, 14, 15, and 17 the tube was heated each day up to about 190°, and curves drawn showing the relation between the pressure and temperature. These curves did not show a very good agreement, from the uncertainty as to corrections above mentioned ; and I therefore will only state that the effect of the heating on the 13th was to reduce the pressure difference to 2 millim., on the 14th to 1·5 millim., on the 15th to ·6. On each day the heating took place during five hours or thereabouts, and the tube was maintained at its highest temperature for about an hour. On August 17th the tube was exposed to a temperature of 200° C. for six hours, and then kept at 110° all night ; and then, on August 18th, again heated to 200° C. for five hours. When the tube was cold, on August 19th, the effect had entirely disappeared, the mercury standing at the same height in both limbs of the tube. On August 21st recombination appeared to have taken place to the extent of ·5 millim., and then this disappeared again between August 21st and September 3rd. No further change having taken place by September 20th, the tube was finally disconnected, and the following conclusions were provisionally noted from a consideration of its behaviour.

1. A compound is formed when the electric discharge is passed over a mixture of mercury and nitrogen at a pressure of about 8 millim. The action commencing slowly, and increasing in velocity till it reaches a maximum, then decreasing, but continuing slowly till at least seven-eighths of the nitrogen is absorbed, the mercury being in excess.

2. The compound formed is brownish at first, but as time goes on it becomes black, probably owing to a continual increase in the quantity of mercury deposited with it.

3. The compound decomposes with crepitation at a temperature of about 200° C. (very rough).

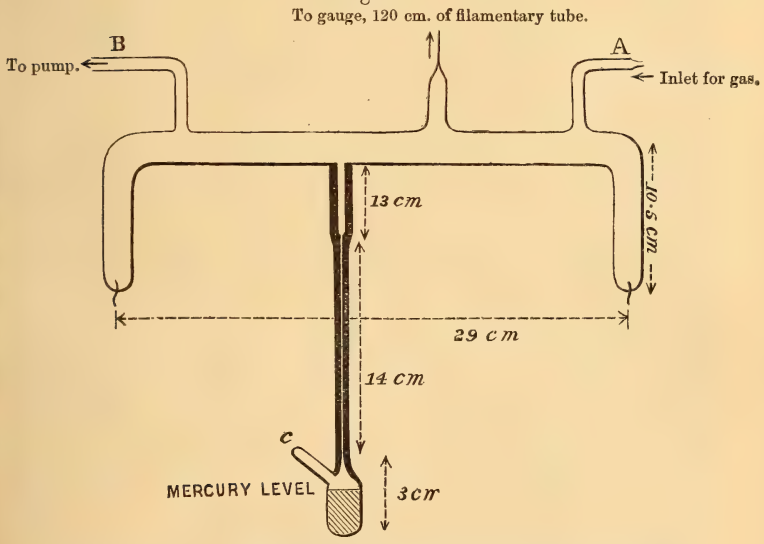
4. The compound is probably identical with the trimercuramine of Plantamour.

5. It behaves as a dissociable compound on heating and cooling, and can finally be entirely decomposed by repeating the heating and cooling often enough.

6. An attempt to get the dissociation curve with such accuracy as would allow the application of analysis failed, through the want of a preliminary determination of the relative capacity of tube and gauge.

It now became necessary to repeat the experiment under

Fig. 2.



Inside diameter of main tube 1·5 cm.; thickness of walls ·15 cm.

slightly changed conditions, so that new facts might present themselves and the previous results be controlled. I decided to make a tube of such a kind that I could begin by sparking it so that the sparks only passed through nitrogen, and then, after a sufficient interval of time and at any convenient opportunity, introduce mercury with a view to observing the modified action. In order to vary the conditions, the whole drying apparatus up to the sulphuric-acid tube was pumped out afresh and filled with gas, which passed through the reagents very slowly. This process occupied two days, one day and a half it took to exhaust the vessels, and half a day

(5 hours) for the gas to flow in. It will be convenient here to describe the tube employed, though the dimensions given are taken from a later experiment, which was supposed to be a repetition of the one in question; the dimensions of this tube may therefore be in error by a few per cent., but the actual dimensions are not of much importance. The ends of the tube dip down into mercury cups (not shown) so as to protect the part where the wires enter from leakage. The mercury pocket in the tube which forms the subject of the diagram (fig. 2) is attached to the spark-tube by means of a capillary tube 14 centim. long.

This capillary tube was the finest piece of thermometer tubing I actually happened to have by me, and was, as I should imagine, about ·1 millim. in diameter *. In preparing the tube after the final filling, the inlet at A is fused off, and when the proper pressure is reached the pump connexion at B is sealed, and afterwards, in two or three hours' time, the connecting tube of the mercury gauge.

September 10–19. These days were spent in abortive attempts to get tubes of the pattern described to submit to having their electrodes white-hot for two or three hours without fracturing the glass.

September 19. Tube 5, as described, sealed off at 8·7 millim. The mercury was put in hot through a side-tube, but was not boiled *in situ* in order to avoid getting vapour into the spark-tube. In order to avoid the presence of air-bubbles between the mercury and the glass, the tube at C was at first about 8 centim. long, and was drawn down to a fine point, where it was fused off. The apparatus was then filled with nitrogen and well heated when containing a nitrogen vacuum, especial care being devoted to the mercury pocket. Nitrogen was then admitted at more than atmospheric pressure, and finally the end of the tube was broken off near C and the mercury run in as quickly as possible from a fine funnel reaching to the bottom of the pocket. The tube at C was then sealed, and the mercury warmed again to perhaps 100° C. and the visible bubbles displaced, the tube being of course vacuous.

Sept. 21. The mercury in the gauge was accurately at the same height in both limbs. Sparked for five hours with the best kind of sparks; no effect.

Sept. 22. Sparked four hours with an air-break in circuit just sufficient to stop the spark but not the brush-discharge across the air-break. It was noticed that luminosity went

* This capillary tube was part of the later arrangements. In the tube under discussion its place was taken by a tube 2 millim. in diameter and only about 6 centim. long.

down the tube to the mercury, and was much increased by touching the outside of the tube near the mercury. This discharge, of course, was small compared with the discharge in the main tube. There was no effect on the gauge.

Sept. 23. Sparked with rather large sparks $6\frac{1}{2}$ hours. No effect.

Sept. 24. Sparked strongly, so as to make the tube warm, for $6\frac{1}{2}$ hours. No effect.

Sept. 25. The mercury boiled up into tube. This led to the gauge showing a real increase of pressure of a little less than ·1 millim.; I attribute this to gas from the sides of the tube between it and the mercury. Sparked strongly for $5\frac{3}{4}$ hours; when all was cold the pressure excess had grown to about ·2 millim., *i. e.* in a direction contrary to the one expected.

Sept. 26. Discharge on for $6\frac{1}{2}$ hours fairly strong, so as to warm tube perceptibly. The gauge then showed the same pressure on each side.

Sept. 27. A wet paper band round that part of the tube where the mercury was most thickly condensed. Sparked four hours (?). No effect.

Sept. 28. Ditto 3 hours. No effect.

Sept. 29. Faint sparks for 5 hours; wet paper band, as before. No effect.

Oct. 1. Temperature being more rigorously equal, and gauge carefully tapped, there is a shrinkage of about ·1 millim. Sparked six hours with faint sparks and wet paper round tube. No effect

Oct. 2. Strong current on 6 hours. Looking the next day (October 3rd), a faint yellow tinge was observed round the mercury drops, and the gauge showed ·8 millim. difference of pressure. Sparked hard 6 hours; the mercury was now obviously attacked, and when examined on October 3rd it was found that the pressure difference amounted to 3·2 millim. Sparked 3 hours with full discharge; this increased the effect to 6 millim., and in another $4\frac{1}{2}$ hours the discharge had become splendidly golden, the resistance in the tube small, and the tube was fluorescing strongly (a sign of mercury vapour). Effect increased to about 7 millim. The experiment was then interrupted by the cracking of the tube.

No opportunity for examining the deposit occurred till November 16th, *i. e.* for more than a month. The tube was then cut into bits, and it was observed that the deposit had become partly incrusted with some whitish incrustation. On trying to produce an explosion the experiment failed, and it was obvious that the film had quite decomposed. It is to be noted that the mercury was only attacked with difficulty.

Tube 6.—Dec. 5, 1891. This is the tube shown in fig. 2. All drying apparatus exhausted twice; tube prepared by a steady discharge during December 11th; left till 14th to test for leaks, when it was found that the whole apparatus was air-tight. Tube again sparked hard all December 14th with best pump-vacuum attainable. Electrodes at a bright red heat for $1\frac{1}{2}$ hours; mercury separated by long tube and boiled in pocket. Sealed off at about 6 millim. pressure on December 15th.

Dec. 16. Sparked 2 hours through capillary water resistance; tube slightly warm. No effect.

Dec. 17. Sparked so as to produce a yellow glow for 3 hours and by small blue sparks for 1 hour. No effect.

Dec. 18. Sparked with fairly strong discharge for 8 hours. Tube too warm to read: so left till December 31st, when it was found that the tube pressure had diminished by ·2 millim. This led to an examination of the tube by holding a sheet of white paper behind it; and it was found that a bronze-coloured film had formed where mercury had condensed near the top of the capillary tube. The mercury within the sphere of action was only the most minute trace. Sparked 3 hours and on.

Dec. 22. Effect about ·3 millim. Sparked for about an hour, and then on careful examination it was found that the glow was actually passing down the tube to the mercury. It was clearly of no use to go on with the experiment in this way, and consequently the mercury was boiled into the tube and the spark turned on. The effect diminished during the boiling from ·35 millim. to ·3 millim. Sparked then for 5 hours; effect increased to 1·2 millim.

Dec. 26. Sparked 4 hours. Effect 2·4 millim.

Dec. 27. Ditto 3 hours. Effect 4·3 millim.

Dec. 28. Sparked for one hour, when it was noticed that the tube-resistance had increased and the gauge showed 5·38 millim. of effect; hence the tube is nearly empty. On first turning on the spark, the illumination began by being strong for about one minute. The striæ were well marked, and the mercury spectrum prominent. After about one minute the luminosity diminished to that corresponding to faint blue sparks. In twenty minutes the tube was again hot and fairly luminous, and continued with luminous sparks and rising temperature for 35 minutes: the gauge showed that the rise of temperature (?) was producing an increase of pressure. Tube cooled for one hour, when it was found that the excessive sparking had at last cracked the tube near the platinum wire, and that some mercury had been drawn in. The tube was then cut into bits, and one was heated in a test-tube in a

glycerine bath with the same precautions exactly as one uses in taking a melting-point. I extract the following account from my note-book *verbatim:*—"I could not detect any change till about 230° C., at which temperature quiet decomposition set in, and was complete and the tube clean at 235°. A considerable portion of the thermometer stem was outside the bath, though it did not begin to register till above 110°. Making all allowances, the temperatures might on this account have been anything less than 5° above those given. The temperature rose very slowly, and the glycerine was kept well stirred by a crescent-shaped stirrer of zinc. Experiments on other bits of the tube were made by heating them in the bare flame. In two of these (out of about four) there was a distinct crepitation, but I did not note any flash, though that the decomposition when once started ran very rapidly over the whole mirror was well seen in all the experiments. The deposit suddenly brightened with a puff of vapour. I could detect no nitrous smell. The temperature must have been 200° C. in all cases. The platinum deposits were enormous, and the electrodes torn up in all directions as described by Edison."

These experiments may be considered to settle the question of the cause of the effect observed by Professor Thomson and myself in 1885 and 1886. No trace of the effect was ever found unless the mercury was attacked; and, contrariwise, the mercury was never seen to be attacked without the "effect" making its appearance. It is curious to note the difference in the readiness with which the action can be brought about, even when all the circumstances of the experiments appear to be identical. It is for this reason that I imagine that the reaction requires the intervention of minute traces of some third substance, and the actual amount of these traces differs in different experiments. When the reaction once commences it goes on with increasing rapidity till near the end, and apparently faster the more powerful the discharge. One experiment appears to indicate that even after the trimercuramine (?) is decomposed its constituents are in a state of "labile" equilibrium with respect to one another, and combine slightly or separate according to some set of circumstances which I cannot assign. It is curious, too, that the dissociation should be so irreversible. Unless the mercury vapour continually liberated is removed from the sphere of action—by combination with the platinum deposit, for instance—I cannot understand the effect of repeated heating; and, indeed, I consider that the suggestion just made is very possibly the true explanation.

The condensation of nitrogen, therefore, at ordinary temperatures has not been observed; but it is possible that it may

occur at low temperatures. For this purpose I prepared

Tube 7, which is figured in the Plate in the position it occupied before it was sealed off. This tube was prepared with even more than the usual care. Thus, the cleaning of the tube occupied two days and the final rinsing was accomplished by means of some thrice-distilled water from the platinum and gold still. This water ran into the tube direct from the still. The electrodes were prepared by sparking during five hours with a discharge sufficient to make them red-hot, during which time the tube was thrice filled and exhausted. The next day the tube was heated twice, and on each occasion about 500 cub. centim. of gas were passed through it; after which it was exhausted as far as possible (in an hour), and then the final charge was allowed to enter. The tube was sealed off at 8·7 millim. pressure, and then put in salt and pounded ice and kept at $-14°$ C. by means of frequent stirring and the addition of fresh ice and salt. Sparked 2 hours with effective sparks: no effect. (The effect was looked for the next day, when the temperatures were equalized, but was not observed.)

Jan. 2. Sparked for 2 hours at about $-10°$ C., all kinds of sparks. No effect.

The filamentary tube was then replaced by a wider one, as it was observed that the gauge only acted very slowly owing to the extreme fineness of the filamentary tube. The spark-tube then required to be pumped out and prepared afresh, except for the heating of the electrodes, which, however, incidentally took place.

Jan. 4. Sparked $1\frac{1}{4}$ hours at $-10°$ C. No effect.

Jan. 6. Sparked 7 hours at a mean temperature of $-8°$ C.; various sparks. No effect.

Jan. 7. Observed again, at very uniform temperatures. Still no effect.

Jan. 12. Ditto.

The conclusion is that no effect is produced on nitrogen, so far as condensation goes, by sparking it at a temperature of about $-10°$ C. and at a pressure of 8·2 millim.

Summary of Results.

1. Nitrogen can be prepared by a continuous process in a state of great purity.

2. Nitrogen so prepared cannot be caused to condense by any available kind of spark down to a temperature of $-10°$ C. and a pressure of about 8 millim.

3. When mercury is present, a compound of mercury and

nitrogen is formed. This compound is probably identical with the nitride obtained by Plantamour.

4. The rate of formation of this nitride, other things being the same, is so irregular as to suggest that its formation is due to the interaction of an otherwise inappreciable trace of some other substance.

5. This compound is dissociable; but under the circumstances of the experiment the dissociation process is not entirely reversible, since sufficient heating will permanently destroy the compound.

6. There are changes in the appearance of the discharge in nitrogen which can be brought about by very slight variations of temperature, and possibly of electromotive force, for which, so far as I know, no explanation is at present forthcoming.

Sydney, August 5, 1892.

II. *On the Refraction of Rays of Great Wave-length in Rock-salt, Sylvite, and Fluorite.* By Heinrich Rubens and Benj. W. Snow*.

[Plate II.]

In volume xl. of Wiedemann's *Annalen* one of the present authors recently described a method whereby a knowledge of the dispersion of rays in the infra-red may be easily obtained. With the aid of this device the dependence of the index of refraction upon the wave-length was determined for sixteen materials; viz. for nine different samples of glass, for water, carbon disulphide, xylol, benzol, quartz, rock-salt, and fluorite. Inasmuch as in this paper is given a minute description of the methods employed, it will suffice here briefly to refer to the main features of the method of procedure followed in the present determination.

The rays from the zirconia burner of Linnemann, after being reflected from the front and the rear surfaces of a thin plate of air, enclosed between two parallel glass planes, were then concentrated upon the slit of a spectrometer, by which means two beams of light were produced, capable of mutual interference, so that the otherwise continuous spectrum of the incandescent zirconia plate was crossed by a series of vertical interference-bands. The wave-length λ of each such dark band, multiplied by a certain whole number m, always equals the product of twice the thickness d of the layer of air and the cosine of the angle of incidence i of the rays. With the aid

* Communicated by the Authors.

of the Fraunhofer lines the wave-lengths of the interference-bands were determined for the visible portion of the spectrum, and from these data were calculated the order m of each dark band and the product $K = 2d \cos i$. The knowledge of these two constants proved, then, sufficient to determine also the wave-lengths of the interference-bands in the infra-red.

The positions of these latter were obtained by allowing the sensitive filament of a linear bolometer to wander through the spectrum, and plotting the observed galvanometer-deflexions as a function of the angular deviation. The interference-bands are then recognized as minima or maxima in the curve. In this way, for a series of angular deviations may be determined the corresponding indices of refraction; that is, a number of points in the $n-\lambda$ plane determined, which, when joined by a smooth curve, give the curve of dispersion for the material examined.

In the majority of the bodies thus investigated, the limit of the region in the infra-red capable of being explored was prescribed by the absorption, which increases rapidly with increasing wave-lengths. In two cases alone, viz. when working with rock-salt and with fluorite, were the investigations discontinued at wave-lengths $\lambda = 5{\cdot}7\,\mu$ and $\lambda = 3{\cdot}3\,\mu$ respectively, before the region of strong absorption was reached. This was rendered necessary by the fact that the apparatus employed proved to be insufficiently sensitive to measure the exceedingly feeble energy found in the spectrum of the zirconia burner at these long wave-lengths.

As a means of continuing the investigation beyond this point two ways of improvement suggested themselves. At first we thought it possible to increase the energy of the source of light, but all endeavours to attain this end proved of no avail. The use of the electric arc for this purpose was, after a short but thorough trial, discontinued. Even arc lamps of unusually good regulation, when supplied by the almost perfectly constant current of the Berlin Central Station, gave a radiation too fluctuating to be used in place of the zirconia light. The regulation of the arc by hand was also tried, but also without success. The use, moreover, of a zirconia burner of nearly double the dimensions of the former resulted in only a feeble increase in the energy, while a series of new difficulties was thereby introduced, such as the melting of the platinum cell, a greater consumption of gas, &c. We concluded, therefore, for the further investigation, to retain the source of light in its original form, and to make better use of the energy here at hand by increasing as far as possible the sensitiveness of the measuring apparatus.

The first change toward the accomplishment of this end was effected in the substitution of two plane surfaces of larger dimensions in place of the reflecting plates formerly used. For this purpose the optical firm of Carl Zeis, of Jena, most generously provided us with two plates with plane surfaces, 4 centim. square and 1 centim. thick, one of crown glass and the other of fluorite. The plates were set in metal frames, and the distance between them regulated by a system of screws, as in the former case. With the exception of the extreme edges both plates were ground to a truly plane surface. A rectangular opening in a diaphragm, placed in the path of the rays, allowed only light to enter the slit of the spectroscope which had been reflected from the central portion of the plates. The interference-bands thus produced were unusually sharp, as can be seen from the pronounced minima of the curves in figs. 1, 2, and 3 (Plate II.), which represent the three different energy-spectra. Hardly need it be mentioned that in the following experiments the entire optical system consisted wholly of rock-salt and fluorite.

The delicacy of the bolometer was increased chiefly by using a galvanometer of the highest degree of sensitiveness which one of us had constructed, and which will be described in detail in a forthcoming paper. The coils of the galvanometer in series measured 140 ohms resistance. When the period of the needle was reduced for the single swing to 10 seconds, one millimetre deflexion on the scale indicated a current of $1{\cdot}3 \times 10^{-11}$ ampere. With this degree of astaticism the zero-point of the needle was perfectly constant.

The bolometer with which the following determinations were made is described as No. 2 in the previous paper. It consisted of two strips of platinum, 12 millim. long and 0·05 millim. wide, each having about 80 ohms resistance, only one of them being exposed to radiation. With the aid of the new galvanometer we were able to trace a sensitiveness of 0·000003° C. per millimetre deflexion. A standard candle one metre distant produced a deflexion of 400 millim.

With the exception of the changes here mentioned all pieces of apparatus were identical with those formerly described. The relative positions, moreover, of the instrument, as well as the manner and the order in which the operations were performed, were retained unchanged. We can therefore pass at once to the results of our observations.

Measurements were made upon the three materials so well known for their diathermanous properties—rock-salt, sylvite, and fluorite.

I. *Rock-salt.*

We had at our disposal a prism of this mineral having a triangular base $3\frac{1}{2}$ centim. on each side and $4\frac{1}{2}$ centim. in height. Before being used the prism was freshly polished and its refracting angle redetermined. The observations with the bolometer gave the energy spectrum represented in fig. 1, Pl. II. The positions of the maxima and minima were corrected, as in the paper cited above, with the aid of the enveloping curve, whereby the points of contact of the two curves were used without further modification as the characteristic points in question. As the theory shows, this method gives a closer approximation to the quantities required than the method by construction given in the former paper. But little weight, however, is to be attached to the superiority of this modification, as both methods lead to results which are identical to the fourth decimal place.

Inasmuch as the present investigation was undertaken expressly for the purpose of extending measurements as far as possible into the infra-red, we were compelled to use a comparatively thick layer of air for reflecting the interfering beams of light, which brought the interference-bands in the spectrum very near together. It was quickly found, however, that even the narrow width of the bolometer and the impurity of the spectrum, caused by the aberration of the lenses, placed a limit beyond which the further reduction of the breadth of the interference-bands could not be carried. With the feeble dispersion of the materials used, this limit was practically reached when the visible spectrum was crossed by seven or eight interference-bands, which gave a value to the constant $K=2d\cos i$ of about $8{\cdot}5\mu$. According to this, the minimum of the first order, which is the farthest possible attainable point in the infra-red, has a wave-length $\lambda=8{\cdot}5\mu$. Then follow the maximum of the second order and the corresponding minimum, which have wave-lengths $\lambda=5{\cdot}7\mu$ and $\lambda=4{\cdot}3\mu$ respectively. Although the curvature of the curve of dispersion in this region is slight, it seems to us, nevertheless, desirable to add, for greater accuracy in our measurements, other possible points to the small number already obtained. In order to attain this end, we found it advantageous to use not only the corrected positions of the maxima and minima and their corresponding wave-lengths for plotting the curve of dispersion, but also the points of intersection of the energy curve $G=f(\alpha)$ (see fig. 1) with the curve of mean energy $R=f(\alpha)$, since the wave-lengths corresponding to the abscissæ of these points are easily calculated. This

latter curve might have been observed directly, had the distance between the plates enclosing the reflecting layer of air been sufficiently increased. This curve $R=f(\alpha)$, which represents the distribution of energy when no interference is present, can be constructed, however, with sufficient accuracy, when at each point an ordinate is erected equal to the mean of the ordinates of the corresponding points of the enveloper, P and Q. If the curve $G=f(\alpha)$ is intersected at any point by the curve $R=f(\alpha)$, then the amplitude for the abscissa of this point must have the same magnitude which it would have attained had a superposition of the energy of the two beams taken place without interference.

The vibratory motion of the two beams whose amplitude and period are A and T respectively, may be represented by the equations

$$y_1=A\sin 2\pi\left(\frac{t}{T}-\frac{x}{\lambda}\right),$$

$$y_2=A\sin 2\pi\left(\frac{t}{T}-\frac{x+K+\frac{\lambda}{2}}{\lambda}\right).$$

They unite to form the ray

$$Y=2A\cos\frac{\pi\left(K+\frac{\lambda}{2}\right)}{\lambda}\sin 2\pi\left(\frac{t}{T}-\frac{x+\frac{K}{2}+\frac{\lambda}{4}}{\lambda}\right)$$

$$=2A\sin\frac{\pi K}{\lambda}\sin 2\pi\left(\frac{t}{T}-\frac{x+\frac{K}{2}+\frac{\lambda}{4}}{\lambda}\right).$$

It follows from what has been said above that, for the abscissa of the point of intersection of the two curves R and G, the amplitude of the beam Y, viz. $2A\sin\frac{\pi K}{\lambda}$, must equal $\pm A\sqrt{2}$. λ is accordingly determined from the equation

$$\sin\frac{\pi K}{\lambda}=\pm\tfrac{1}{2}\sqrt{2},$$

$$\frac{\pi K}{\lambda}=\frac{\pi}{4},\ \frac{3\pi}{4},\ \frac{5\pi}{4}\ldots\frac{(2n+1)\pi}{4},$$

where n is any whole number. The wave-length, therefore, of each point of intersection is given by the equation

$$\lambda=\frac{4K}{2n+1}.$$

A knowledge of the order of the adjacent maxima and minima gives at once an interpretation to the quantity n. If

the point of intersection in question lies in such a way that the adjacent minimum (mth order) lies on the side of the longer wave-lengths, and the adjacent maximum on the side of the shorter wave-lengths, then $n=2m$.

The introduction of these points in the calculation of the curve of dispersion made it possible for us to conduct the observations with interference-bands as broad as were necessary, and at the same time to obtain a sufficiently great number of points to enable us to ascertain the character of the curve of dispersion with nearly the same degree of accuracy as in those portions of the spectrum lying but little beyond the reach of the eye.

At this point mention should be made of a peculiarity of the energy-curve, which may be observed in the drawing (fig. 1). The deflexions of the galvanometer, at the point of the last minimum a_{11}, not only sink to zero, but even assume negative values. The cause of this singularity, which also appears to a smaller degree in the energy-curve of fluorite, is to be found in the fact that the second unilluminated arm of the bolometer, which was placed in the apparatus within a casing of hard-rubber, notwithstanding this covering received upon its surface a greater amount of energy than the first arm, which was exposed to the direct radiation. The plausibility of this explanation is increased when we remember that the covered resistance is then at a portion of the spectrum in which the mean energy is 50 times greater than in the neighbourhood of the minimum a_{11}, and that ebonite is not opaque to thermal radiation of great wave-length.

In the following Table are found the results of the observed indices of refraction and wave-lengths. The first column, entitled "Name," gives the quality of the characteristic point in question, as Fraunhofer line, minimum (a), maximum (b), or point of intersection (c) of the curves G and R; the second column contains the angle of deviation α as measured on the graduated circle; the third contains the index of refraction n, calculated from the refracting angle ϕ and the angle of deviation α according to the formula

$$n=\frac{\sin\frac{\phi+\alpha}{2}}{\sin\frac{\phi}{2}};$$

the fourth column contains finally the wave-length which is calculated from the order m of the interference-band and the constant $K=2d\cos i$. The curve of dispersion plotted from the data of this Table is found in fig. 4, a.

TABLE I.

Refracting Angle of the Rock-salt Prism, $\phi = 60° \ 2'$.
$K = 8{\cdot}307\mu$; a_1 is 11th Order.

Name.	a.		n.	λ.
	°	′		μ.
H_γ	42	37	1·5607	0·434
F	41	56	1·5531	0·485
D		7	1·5441	0·589
C	40	47	1·5404	0·656
a_1		29	1·5370	0·755
b_1		22½	1·5358	0·790
a_2		16½	1·5347	0·831
b_2		11½	1·5337	0·876
a_3		7	1·5329	0·923
b_3		2½	1·5321	0·978
a_4	39	58	1·5313	1·035
b_4		54½	1·5305	1·107
a_5		51	1·5299	1·186
b_5		47½	1·5293	1·277
a_6		44	1·5286	1·384
b_6		41	1·5280	1·511
a_7		38	1·5275	1·660
b_7		35	1·5270	1·845
a_8		32	1·5264	2·076
b_8		28	1·5257	2·372
a_9		22½	1·5247	2·771
c_1		18	1·5239	3·022
b_9		13½	1·5230	3·320
c_2		7	1·5217	3·690
a_{10}		2	1·5208	4·150
c_3	38	56	1·5197	4·745
b_{10}		49	1·5184	5·540
c_4		37½	1·5163	6·647
a_{11}		24	1·5138	8·307

It is well known that Professor Langley*, by a method wholly different from the one here described, was able to follow the dispersion in rock-salt to a wave-length $\lambda = 5{\cdot}3\mu$. He found, in these experiments, that the curve of dispersion from about $\lambda = 2\mu$ on followed very nearly a straight line. Owing to the fact that even with the elaborate means at hand he was unable to extend measurements by his method farther than this in the direction of the long wave-lengths, he concluded to extend this straight line throughout the still more distant region of the infra-red in which his observations were taken.

Many theoretical objections are at once suggested by so extensive an exterpolation. Among these criticisms may be

* *Ann. de Chim. et de Phys.* [6] ix. p. 433 (1886).

mentioned one in particular, that, from a definite wave-length on, the indices of refraction would assume negative values, which points to an utter impossibility. There remained, however, the possibility that within the limits of Professor Langley's measurements of energy, the straight line exterpolation gave results which were at least a first approximation to the true value. A glance at the curve (fig. 4, *a*) shows, on the other hand, that in reality this is not the case. Indeed it is true that our own curve of dispersion tends toward a straight line until a point is reached almost as distant as $\lambda=5\mu$; but at $\lambda=5\mu$ the curve begins gradually to lessen its inclination to the horizontal axis of wave-lengths; and at $\lambda=8\mu$ the effect of this curvature is so considerable that a straight line exterpolation carried from $\lambda=5\mu$ on to this point would introduce an error in the determination of wave-length not less than 1μ.

In the following Table a comparison is made between our results and those of Professor Langley. It is to be noticed that his curve, as far as this is plotted from his observations, agrees fairly well with our own, but that his values given by exterpolation differ widely from those observed by us, and that their difference increases as the wave-lengths become longer. There are also added here for completeness the data obtained from the previous paper. That an easier comparison may be made with Langley's figures, the wave-lengths selected increase by multiples of $\lambda_D=0{\cdot}589\mu$.

TABLE II.

Wave-length.	n (Langley).		n (Rubens).	n (Rubens & Snow).	n (Langley) − n (Rub. & Sn.).
μ					
1. $\lambda_D=0{\cdot}589$	1·5442	Observed.	1·5441	1·5441	0·0001
2. $\lambda_D=1{\cdot}178$	1·5301		1·5300	1·5301	0
3. $\lambda_D=1{\cdot}767$	1·5272		1·5269	1·5272	0
4. $\lambda_D=2{\cdot}356$	1·5254		1·5253	1·5256	−0·0002
5. $\lambda_D=2{\cdot}945$	1·5243		1·5241	1·5240	+0·0003
6. $\lambda_D=3{\cdot}534$	1·5227		1·5227	1·5226	1
7. $\lambda_D=4{\cdot}123$	1·5215		1·5214	1·5212	3
8. $\lambda_D=4{\cdot}712$	1·5201		1·5202	1·5200	1
9. $\lambda_D=5{\cdot}301$	1·5186		1·5189	1·5188	−0·0002
10. $\lambda_D=5{\cdot}890$	1·5172	Exterpolated.	...	1·5177	5
11. $\lambda_D=6{\cdot}480$	1·5158		...	1·5166	8
12. $\lambda_D=7{\cdot}070$	1·5144		...	1·5157	13
13. $\lambda_D=7{\cdot}66$	1·5129		...	1·5148	19
14. $\lambda_D=8{\cdot}25$	1·5115		...	1·5138	23

The values, therefore, attributed by Professor Langley* to the wave-lengths in that region of the spectrum lying between $\lambda=0$ and $\lambda=5\mu$ are undoubtedly correct. Beyond this limit, however, at least as far as $\lambda=8{\cdot}3\mu$, the values assumed are too small, but it is not impossible that when still greater wave-lengths are reached the sign of the error may change. The results, nevertheless, of his observations remain of the greatest interest, since it will be easily possible to apply a correction to the wave-lengths as soon as the dispersion in rock-salt can be followed to sufficiently small indices of refraction.

Sylvite.

The behaviour of rock-salt is in every respect similar to that of the mineral sylvite, to which it stands in close chemical relation. There was placed at our disposal a prism of this material, 14 millim. at the base and 20 millim. in height. The surfaces of this prism were so well polished that the refracting angle could be determined to within 0·5 minute.

In fig. 2 the observed galvanometer-deflexions are plotted as functions of the angular deviation of the arm of the bolometer. From this curve is computed the table of dispersion in the manner described above. Corresponding to this is plotted the curve of dispersion (fig. 4, *b*).

TABLE III.

Refracting Angle of the Prism of Sylvite, $\phi=59^\circ\ 54'$.
$K=8{\cdot}022\,\mu$; a_1 is 10th Order.

Name.	*a*.	*n*.	λ.	Name.	*a*.	*n*.	λ.
	° ′		μ		° ′		μ
H_γ ...	37 30	1·5048	0·434	b_5	35 5	1·4766	1·458
F	36 55	1·4981	0·486	a_6	2½	1·4761	1·603
D	13½	1·4900	0·589	b_6	34 59½	1·4755	1·781
C	35 57	1·4868	0·656	a_7	56½	1·4749	2·005
a_1	37	1·4829	0·802	b_7	53	1·4742	2·291
b_1	32	1·4819	0·845	a_8	48	1·4732	2·673
a_2	27	1·4809	0·893	b_8	43	1·4722	3·209
b_2	23½	1·4802	0·944	c_1	40½	1·4717	3·561
a_3	20	1·4795	1·003	a_9	38	1·4712	4·011
b_3	16½	1·4789	1·070	c_2	35½	1·4708	4·577
a_4	13	1·4782	1·145	b_9	32	1·4701	5·345
b_4	10	1·4776	1·234	c_3	28	1·4693	6·412
a_5	7½	1·4771	1·337	a_{10} ...	22	1·4681	8·022

* Langley, Sill. Journ. [3] xxxi. pp. 1–22, 1886; further [3] xxxii. pp. 83–106, 1886, and [3] xxxviii. pp. 421–440; Phil. Mag. xxvi. p. 505, 1888. The same is true of t he paper of Ångström, *Öfversigt af Kongl. Vet.-Akad. Förhandl.* ix. p. 549, 1889, and vii. p. 331, 1890, and W. H. Julius, *Arch. Néerl.* i. pp. 310–384, 1888.

A study of this curve shows that the dispersion in sylvite, which in the visible spectrum is only slightly inferior to that in rock-salt, decreases in a similar manner but far more rapidly than in the latter mineral, so that at wave-length $\lambda = 8\mu$ the dispersion is only about one third of the corresponding dispersion in rock-salt.

Notwithstanding the great durability of this material, and its permanence in moist air as well as its almost perfect transparency to thermal radiations, the exceedingly rapid decrease in the dispersive power of sylvite renders this substance not so well adapted for experiments involving the use of prisms as rock-salt, whose surfaces are only with difficulty kept perfect. In the construction of condensing lenses this difficulty does not occur.

Fluorite.

The prism here examined is the same one which was used in the former investigation. The value of the refracting angle was redetermined and was found to agree very closely with the observations previously made.

For a long time we tried in vain to measure beyond wave-length $\lambda = 3{\cdot}5\,\mu$, the energy-spectrum produced by the fluorite prism. The results of the previous observations show the cause of our failure to be due to the fact that, after a region of comparatively feeble dispersion, the dispersive power of fluorite increases and the energy in this portion of the spectrum becomes proportionally weaker. In order to make further advances, we were finally compelled to open wider the slit of the spectrometer at those places where the radiant energy sank below a measurable quantity. The repetition of this device enabled us to reach a wave-length in the infra-red greater than $\lambda = 8\mu$. In the curve shown in fig. 3, which represents the observed distribution of energy produced by the fluorite prism, the slit was twice opened; the first time from 0·1 millim. to 0·4 millim. when the arm of the bolometer was at a deviation $\alpha = 30° \; 10'$, and a second time from 0·4 millim. to 1·0 millim. at an angle of deviation $\alpha = 28° \; 50'$. By this means the deflexions of the galvanometer were increased fourfold and tenfold respectively. Owing to the greatly increased dispersion and the corresponding increase in the breadth of the interference-bands, this change in the width of the slit did not materially interfere with the sharpness of the bands in this region of the spectrum. Inasmuch as only one side of the slit was movable, a correction had to be applied to the reading of the arm of the bolometer when the slit was opened.

The distribution of energy, as shown in fig. 3, gives a curve whose character is wholly different from the representation of

the energy-spectra produced by rock-salt or sylvite, given in figs. 1 and 2. While in these latter the breadth of the interference-bands increases only slowly as the extreme infra-red is reached, amounting finally to hardly more than double the smallest value, the breadth of these bands varies in the energy-spectrum, as given by the fluorite prism, from 5 minutes to more than $2\frac{1}{2}$ degrees. Corresponding to this peculiar characteristic in the energy-spectrum of fluorite, the quality of the dispersion in this mineral is quite different from that of the materials previously considered.

In the following Table, which contains these data, the indices of refraction are given only to three decimal places. As a result of the very considerable breadth of the interference-bands, it is impossible to locate the position of the characteristic points with the precision attainable in other cases.

TABLE IV.

Refracting Angle of the Fluorite Prism, $\phi = 59° \, 59\frac{1}{2}'$.
$K = 8{\cdot}070\,\mu$; a_1 is 10th Order.

Name.	a.	n.	λ.	Name.	a.	n.	λ.
	° ′		μ		° ′		μ
H_γ ...	32 5	1·4398	0·434	b_5	30 59	1·4267	1·466
F	31 52	1·4372	0·485	a_6	$55\frac{1}{2}$	1·4260	1·613
D	36	1·4340	0·589	b_6	51	1·4250	1·792
C	29	1·4325	0·656	a_7	46	1·4240	2·019
a_1	19	1·4307	0·807	b_7	38	1·4224	2·303
b_1	17	1·4303	0·850	a_8	29	1·4205	2·689
a_2	$14\frac{1}{2}$	1·4299	0·896	b_8	13	1·4174	3·225
b_2	12	1·4294	0·950	a_9	29 46	1·4117	4·035
a_3	10	1·4290	1·009	c_1	29	1·408	4·62
b_3	8	1·4286	1·076	b_9	4	1·403	5·38
a_4	6	1·4281	1·152	c_2	28 30	1·396	6·46
b_4	4	1·4277	1·240	a_{10} ...	27 5	1·378	8·07
a_5	2	1·4272	1·345				

The curve of dispersion, shown in fig. 4, *c*, exhibits more graphically than this table the peculiar character of the dispersion. From this it is seen that the dispersive power of fluorite decreases as far as $\lambda = 2\,\mu$ and then gradually increases, reaching at $\lambda = 8\,\mu$ a value only slightly inferior to the value of the dispersion in the red.

Compared with rock-salt and sylvite, the dispersion of fluorite in the visible spectrum is exceedingly small and unusually great in the infra-red; so that this material is peculiarly well adapted to the production of prismatic heat-spectra, an advantage which is still further increased by the ease with which it can be worked and by the permanence of its surface in the air.

Physical Laboratory, University of Berlin,
June 1892.

III. *Notes on the Construction of a Colour Map.* *By* Walter Baily, *M.A.**

1. In my paper on this subject, read before the Physical Society on April 8 last†, in discussing the method of plotting out the curve giving the mixtures of two spectrum colours, I stated that points in the curve lying in the abnormal or imaginary regions could not be determined by experiment. This I now find is a mistake.

Let S_1 and S_2 be spectrum colours, of which the mixtures are to be represented by points on the curve. The part of the curve lying in the imaginary and abnormal regions is obtained by *subtracting* light of one colour from light of the other colour, and equating the resulting colour to the mixture (if I may use the expression) obtained by *subtracting* white from some other spectrum colour S.

We have

$$n_1S_1 - n_2S_2 = S - xW.$$

This equation does not represent any possible physical experiment, but it may be transformed, without altering the value of any of the quantities, into

$$S + n_2S_2 = n_1S_1 + xW.$$

This last equation means :—Make a colour-patch of S and S_2, and a colour-patch of S_1 and W, and vary the quantities of S_1, S_2, and W until the two patches are similar in colour, and then measure the quantity of white. A line drawn to the left from the position of S, and proportional in length to the quantity of white, will define the position of the required point in the curve.

2. In the map the region on the right of the line of spectrum colours is occupied by all the colours obtained by mixing spectrum colours and white. I suggest that this should be called the Spectral Region. The equation for determining points on the mixture curves in the Spectral Region is

$$n_1S_1 + n_2S_2 = S + xW.$$

The region to the left of the abnormal and imaginary regions is occupied by colours complementary to those in the Spectral Region. I suggest that this should be called the Complementary Region. The equation for determining points

* Communicated by the Physical Society: read October 28, 1892.

† Phil. Mag. June 1892, p. 496.

on the mixture curves in the Complementary Region is

$$S + n_1S_1 + n_2S_2 = xW.$$

The equation for determining points on the mixture curves in the Imaginary and Abnormal Regions has just been shown to be (for one part of the curve)

$$S + n_2S_2 = n_1S_1 + xW,$$

and it is obvious that for the other part it will be

$$S + n_1S_1 = n_2S_2 + xW.$$

3. In defining a colour as compounded of a spectrum colour and white, we have to determine both quality and quantity of the white light.

A colour may be defined by three spectrum colours by means of the equation

$$n_1S_1 + n_2S_2 = n_3S_3 + xW,$$

or of the equation

$$n_1S_1 + n_2S_2 + n_3S_3 = xW.$$

The colour is that obtained when a patch formed in accordance with one side of the equation is made identical with a patch formed in accordance with the other. In this case quantity of white need not be defined, but quality must be defined.

If a colour be defined by four spectrum colours the definition is independent of any convention as to the quality of white light. Let S_1, S_2, S_3, S_4 be four spectrum colours whose wave-lengths are in order of magnitude, then the equation

$$n_1S_1 + n_3S_3 = n_2S_2 + n_4S_4$$

defines a certain colour, which can be obtained by making a patch of S_1 and S_3 identical in colour with one of S_2 and S_4.

IV. *Mountain-Sickness; and Power and Endurance.* *By* R. H. M. Bosanquet, *F.R.S.**

THE account of mountain-sickness at great altitudes, given in Mr. Whymper's work, 'Travels amongst the Great Andes of the Equator,' is of great interest. On reading it, it appeared to me to suggest a simple explanation of the occurrence of mountain-sickness under the circumstances

* Communicated by the Author.

narrated, an explanation consistent with all the facts, including the immunity enjoyed by Mr. Perring (p. 51). I thought the matter too plain for publication. But the appearance of Mr. Dent's article in the 'Nineteenth Century' (Oct. 1892), "Can Mount Everest be ascended?" shows that my point of view has escaped notice. This appears at once from the remark at p. 611: "Men of large vital capacity, with large bones and full-blooded, are the best suited [for the ascent of the highest mountains]." So far as mountain-sickness of the great-altitude type is concerned, this is certainly not true without qualification: the case of Mr. Perring above alluded to is in point.

The body may be compared to a steam-engine and boiler, the food-arrangements being paralleled by a mechanical stoker, such that the supply of fuel can be fed into the reservoir of the stoker in lump quantities, as food is fed into the stomach at meals. The digestion and other internal arrangements, which we may speak of as the "internal feed," pass this on into the place of combustion just as a mechanical stoker does fuel. When food is regularly taken, the internal feed will supply the combustion within the body at a more or less constant rate, not depending on any voluntary action at the moment, but depending on the constitution, on the average amount of food taken at meals, and probably on the efficiency or wastefulness of the internal feed.

The rate of the internal feed must vary enormously in different persons. In men "of large vital capacity, . . . and full-blooded," it will generally be very much larger than in persons of small vital capacity.

Now we can easily suppose an internal feed so copious as to approach, in its requirement of oxygen for its proper combustion, the possible supply afforded by the breathing mechanism. And my suggestion is simply that in cases of great-altitude mountain-sickness, such as Mr. Whymper relates, the diminution of the air-supply reaches a point at which there is not enough oxygen for the consumption of the fuel continually brought forward by the internal feed. Of course, so long as this is the case, disturbance of the system is to be expected from the accumulation of the reducing (oxygen-devouring) substances furnished by the internal feed to the blood. Under these circumstances, food would probably not be taken for a time; the internal feed would after a time be reduced; and an equilibrium of the system set up again founded on a reduced food consumption. And this is precisely what happened, according to Mr. Whymper's account.

On the other hand, Mr. Perring, "rather a debilitated man, and distinctly less robust than ourselves" (p. 51), escaped the sickness. According to my view, the food-supply his system was dealing with was not in excess of what could easily be consumed by the air he breathed, even at the reduced density.

According to this view, while the artificial supply of oxygen advocated by some investigators should be able to give relief, if the oxygen could be got to its work, yet the obvious course is to attack the other element; and by a judicious preliminary course of moderate starvation, combined with light work, to endeavour to bring the system into the required condition of reduced fuel consumption—in fact into the condition at which it arrived in Mr. Whymper's case, through the painful path of the attack of mountain-sickness.

So far I have spoken of what may be called "great-altitude" mountain-sickness. As to the more ordinary form, I am sorry to say I was at one time a sufferer. Experience enabled me to overcome it by adopting a slow uniform measured pace. But, after the disappearance of the agility of youth, for some seasons I always suffered in my first expeditions, even at quite moderate elevations. And I have no doubt whatever that it was due to the system being overtasked; that is to say, when I was endeavouring to do something like, say, $\frac{1}{12}$ of a horse-power for a time far longer than I was capable of, I collapsed, probably not being capable of doing more than, say, $\frac{1}{20}$ of a horse-power for any considerable time, at all events when out of training.

So far I have avoided going into numerical details, as they are not necessary for the general explanation, and they open up an exceedingly wide subject. But I propose now to deal shortly with certain relations of the external work which can be performed by men; this is conveniently reckoned in terms of "horse-power."

One "horse-power" is commonly defined as 550 footpounds per second, without qualification. When recently horses were replaced by electric motors on certain tramways, it was generally considered a surprise that motors of about 35 H.P., as above defined, were required to replace the horses. The explanation is that the 550 footpounds per second definition was based on the average effort that horses could exert for a considerable time. The output of power of a horse on such occasions as drawing a load up a sharp hill must be quite ten times a nominal horse-power. And the machine is required to be able to replace the greatest effort of which, say, 3 horses are capable.

Similarly, consider a man weighing 12 stone. According to a well-known mountaineering datum, he may lift his weight 1000 feet per hour for many hours. Under these circumstances he is doing about $\frac{1}{12}$ of a nominal horse-power.

Certain experiments on the treadmill gave $\frac{1}{8}$ horse-power external work, maintained for $3\frac{1}{2}$ hours.

But any ordinary person can do a whole horse-power, if the time of the effort be short enough. Take a man weighing 12 stone = 168 lb. If he raise his weight a little over 3 feet per second, he is doing a horse-power of work. (For 550/168 = 3·27, or a little more than $3\frac{1}{4}$.) Now any ordinary person who can run upstairs two steps at a time can do this easily for a few seconds, and an active person for longer, *but the duration of the effort will not easily exceed a certain fraction of a minute.*

Further, active people can do 2 horse-power, running upstairs at the rate of $6\frac{1}{2}$ feet of ascent per second, for a very few seconds.

It appears, therefore, that the power a man is capable of exerting depends on the duration of the effort.

The following (p. 51) are a few data I have selected as the basis for a numerical law.

The law adopted is that the time of duration of effort (or the "endurance") varies inversely as the cube of the power exerted, supposed uniform. Or, conversely, that the power which can be exerted for a given time varies inversely as the cube root of the time (or of the "endurance").

Of course the numbers here given can only be rough approximations to an average; and we need not be surprised if we find wide divergences in isolated cases.

While the correspondence of the calculated times with the estimates is not in all cases close, the discrepancies are in opposite directions. Further, any considerable change in the assumed law would tend to make the calculated numbers impossible in the one direction or the other. Thus, if we took the fourth power instead of the cube, it would make the tasks at the bottom easier, and that at the top impossible or nearly so, and *vice versâ* if we took the square instead of the cube.

The treadmill datum has been taken as the starting-point, the calculated endurances of the other cases being derived by multiplying $3\frac{1}{2}$ hours by the cubes of the inverse ratios of H.P.

It must be noted that we do not know the average weight of Leslie Stephen's party. I have assumed that this was 12 stone. If not, a correction will be required. It will be seen that their actual endurance appears greatly to exceed

Nature of Data.	Exact H.P.	Approximate H.P.	Calculated endurance.	Estimated or actual endurance.
Mountaineer's rule of 1000 feet per hour. Estimated endurance, say 10 hours	·085	$\frac{1}{12}$	$11^h\ 8^m$	10^h
Leslie Stephen: Dom from Randa. 10,000 feet in 8 hours. (*Ball.*).....	·105	$\frac{1}{10}$	$5^h\ 54^s$	8^h
Datum from treadmill, quoted from Smith by Frankland (Chem. Journ. 1868, p. 42). Reduced by me to English units	$\frac{1}{8}$	$\frac{1}{8}$	$3\frac{1}{2}^h$ (datum).	$3\frac{1}{2}^h$
1 H.P. exerted by ascending at rate of 3·27 feet per second for some fraction of a minute ..	....	1	$24^s{\cdot}6$	Fraction of minute.
2 H.P. exerted by ascending at rate of $6\frac{1}{2}$ feet per second for few seconds.....	....	2	$3^s{\cdot}08$	Few seconds.

that indicated by the law for the power developed. If the average weight were much less the discrepancy would be lessened. But I think I remember seeing Leslie Stephen described somewhere as "the fleetest-footed of all the Alpine brotherhood;" so that probably his party might be expected to show an endurance in excess of the average, at a high speed of ascent.

The bearing of these considerations on the use of such an expression as "horse-power" is important. However convenient it may be as a short name for 550 ft.lbs. per sec., it is clear that no specification of ft.lbs. per sec. can really represent the work of any animal, unless the endurance, or the time for which that power can be maintained, is also specified, and the law connecting the two is known.

V. *Further Data on Colour-blindness.*—No. III. *By* Dr. William Pole, *F.R.S.**

Professor von Helmholtz's *Handbook of Physiological Optics.*

Of all the names that could be mentioned as authorities on the subject of colour-blindness, probably that of von Helmholtz stands the highest, not only from the association of his name with that of Young in the most popular theory of colour-vision, but more especially on account of his monumental *Handbuch der Physiologischen Optik*, which has acquired a classical celebrity. This work appeared at intervals from 1856 to 1866; but scientific knowledge advances much in a quarter of a century, and the learned author is conferring a great boon on the public by giving them a new edition, thoroughly revised and brought up to date. To make it more accessible it is published in separate "Lieferungen," of which seven have appeared, comprising 560 closely printed large octavo pages.

I have been surprised to find how little this new edition is known in England; and as the part treating of colour-blindness is already out, it would be culpable, in offering data on this subject, to omit reference to it, particularly as one of the special objects of this Magazine has always been to call the attention of the English-reading scientific world to important foreign publications. The subject mentioned forms, indeed, but a minute item in the whole treatise; but

* Communicated by the Author.

"*ex pede Herculem*," and I may claim a more extensive discipleship under the great master in another branch of his labours.

The description of colour-blindness which Helmholtz gave in the old edition is so well known that it is only necessary to refer to a few passages bearing on our comparisons with the new one. The author stated (p. 294) that the patients saw in the spectrum only two colours, which they for the most part called blue and yellow, and he mentioned experiments on a patient tried by himself, which proved that for this person's eyesight all colours could be compounded by mixtures of yellow and blue. He then explained how, on Grassmann's principles of colour mixtures, "for an eye which acknowledges trichromic matches, but which confuses red with green, it follows that all the hues which it especially distinguishes may be compounded of two other colours something like (*etwa*) yellow and blue."

The author, however, in further explanation, pointed out why he believed that yellow and blue might not be the colour-sensations really experienced. He said, p. 297 :—

> In the Young hypothesis the colour invisible to the colour-blind eye could naturally be only one of the fundamental colours. . . . Red-blindness would thus be explained on Young's hypothesis by a paralysis of the red-perceiving nerves . . . . . and it follows from this that the red-blind perceive only green, violet, and their mixture, blue.

He also (p. 299) mentioned another class, in regard to whom "it might be conjectured (*kann man vermuthen*) that their defect lay in an insensitiveness of the green-perceiving nerves." These passages, it will be seen, contain the essence of the original application of Young's theory to dichromic vision, which became so popular.

We now turn to the new edition ; and as it is matter of common knowledge that, in the interval of time since the previous publication, the applicability of the hypothesis referred to has been seriously questioned, we look with interest to what is said now on the matter.

We may take it up at page 362, where we find a mathematical investigation by geometry and algebra, to show that if two colours, R and G, appear alike to the colour-blind, there may be found another colour which, though visible to the normal eye, is invisible to them. All this is just as it stands in the old edition ; but now we come to the first change of importance. The author, at the end of the investigation, adds a new passage as follows :

But it is not hereby excluded that this wanting colour might also be wanting to the normal eye, and its weight = 0. That would mean that two of the fundamental sensations of the normal eye would, to the colour-blind person, be excited to equal strength by all exciting causes. In fact, it has recently become probable that the solution of the enigma is to be sought in this direction.

The older attempts to explain colour-blindness proceeded from the first-named assumption, that one of the fundamental sensations was wanting to dichromic eyes. I myself have adopted this in the first edition of this hand-book*.

As Helmholtz is not a person to use language inconsiderately in such a case as this, we may gather much information from this short passage. In the first place he makes it clear that the original hypothesis was not intended as a positive and definite explanation. It was only an "attempt to explain," and it is now characterized as "alt" (old), a word which, as I understand it, does not here mean simply early in time, but carries with it the idea of "aged," "ancient," "antique," "stale," something superseded by "new." The expression often recurs with clearly this meaning. Then the explanation of colour-blindness is called an "enigma"; it is still obscure, and wanting "solution." And thirdly, the passage states that in consequence of some recent events a new solution has become probable in a certain direction. The recent events alluded to have been clearly the more complete evidence acquired as to the facts of dichromic vision; and the new solution, which indeed is already indicated, will be better explained by and by.

It is difficult to construe all this otherwise than as intimating that the author does not now attach much weight to the former explanation, and we shall find, farther on, abundant confirmation of this interpretation.

He, however, thinks it right to reprint the part which contains the "älteren Erklärungsversuche," but he adds now the following new saving clause (p. 366).

Nevertheless (*immerhin*), as it appears doubtful what sensations of the normal eye correspond to the two colour sensations of the dichromic patients, Donders has recommended that, according to

* The important original passages are as follows:—

"Das würde heissen, dass zwei der Grundempfindungen des normalen Auges dem Farbenblinden durch alle Reizmittel gleich stark erregt würden. In der That ist es neuerdings wahrscheinlich geworden, dass in dieser Richtung die Lösung des Räthsels zu suchen ist.

"Die älteren Erklärungsversuche der Farbenblindheit gingen von der erstgenannten Annahme aus, dass den dichromatischen Augen eine der Grundempfindungen fehlte. Ich habe dies in der ersten Auflage dieses Handbuchs selbst angenommen."

the customary expression of painters, the colour corresponding to the red or less refrangible half of the spectrum should be called the *warm* colour, and that of the blue half the *cold* colour; and we will do so in what follows.

At pages 367–8 he remarks on the distinction of the classes of "red-blind" and "green-blind," but more positive opinions are given later.

At pages 368 and 369 we come upon the "new" explanation of colour-blindness already alluded to. The idea of this appears to have arisen with Helmholtz himself at a very early period. In 1860 Edmund Rose pointed out the difficulty of Young's original explanation, stating that after careful examination of 59 colour-blind patients, he found it irreconcilable with the facts observed. In 1867, when the last portions of Helmholtz's work appeared, he noticed Rose's experiments, admitting as an alternative suggestion (p. 848), that "in the case of the congenital colour-blind it might well be imagined that the activity of the nerve-fibres might not be removed, but that the intensity curves of the three kinds of light-sensitive elements might change, whereby a much greater variability in the effect of objective colours on the eye might enter"*.

Leber, in 1873, expanded the idea and put it into a practical form. The great difficulty had been the continually increasing evidence that the warm sensation of the colour-blind corresponded with the normal yellow, and not with red or green as the Young explanation would require; and Leber pointed out that if, instead of abolishing the red or the green element, the two were assumed, by changes in their intensity curves, to coincide, forming yellow, the whole difficulty would vanish. This explanation was afterwards repeated by Fick, and at a later time, 1886, reproduced by König in his communication to the British Association.

Helmholtz takes this up in his new edition apparently with approval, and much matter will be found bearing on it in pages 368 and following, and again at page 376. He thinks that if the green curve has gone over to the red, it will produce the sensations of the "green-blind"; but if the red curve has gone over to the green, it will produce those of the "red-blind," there being, however, less frequent intermediate degrees between the two extremes.

In pages 372 to 374 he applies the same explanation (as Fick had done) to the colour phenomena of the normal

* The new explanation is always ascribed to Leber; this clear anticipation of it by Helmholtz seems hitherto to have escaped attention, even by Dr. König.

retina, and alludes to the analogy between these and colour-blindness.

Helmholtz thinks it right to devote considerable space (pages 376 to 382) to the discussion of the theory of Hering. He considers it a modification of Young's theory, giving a long description of it, illustrated by mathematical formulæ, and he says it will explain the facts of colour combinations as well as, but not better than, Young's theory. Then follows much controversial matter, founded on arguments and statements by Hering, but very little of which affects the question of colour-blindness.

The most important novelty in Helmholtz's second edition is contained in section 21, on *The Intensity of the Sensation of Light*. This section is a long one, extending over nearly 100 pages; and a large portion of it, *i. e.* from pages 401 to 473, is entirely new. It contains a most elaborate essay on "Helligkeit," a word for which we have no perfect equivalent, but which is generally rendered by "brightness" or "luminosity." The matter is principally devoted to the relations between "Helligkeit" and colour, which appear to be exceedingly complicated and difficult; so much so, indeed, that Helmholtz, with the modesty that so often accompanies great knowledge, expresses distrust of his power to deal satisfactorily with them.

Fortunately, however, we have no occasion to speak of these relations, further than as they are connected with *an entirely new determination of the three fundamental colour-sensations*, by a method in which "Helligkeit" (which for this purpose I translate as "luminosity") takes a part. This investigation may be said to begin on page 444, with a dissertation, "On the relations between Sensitiveness to Colour and Sensitiveness to Luminosity." The author raises the question how far observations on the spectral colours, having these elements in view, will bear on the nature of the three physiological colour-sensations, and having satisfied himself on this point he undertakes the investigation.

I can only give (and it would not be right to do more) the barest outline of this interesting but difficult and complicated problem. It adopts in the first place the view of the fundamental sensations applied shortly before by König and Dieterici in attempting a similar inquiry. They had analysed the spectral hues by a great mass of experiments, using three "*Elemental* colours" R, G, V, taken from the two ends and the middle of the spectrum, by combinations of which every other spectral hue could be produced. These, on the

old plan, would have been called the primary colours; but here they were only considered as preliminary elements; the new fundamental colours, say x, y, and z, being dependent on them and connected with them by linear equations: thus

$$x = a_1 . \mathrm{R} + b_1 . \mathrm{G} + c_1 . \mathrm{V},$$

$$y = a_2 . \mathrm{R} + b_2 . \mathrm{G} + c_2 . \mathrm{V},$$

$$z = a_3 . \mathrm{R} + b_3 . \mathrm{G} + c_3 . \mathrm{V}.$$

The nine coefficients having to be hereafter determined, making, in each line,

$$a + b + c = 1.$$

To arrive at these constants appears the *crux* of the problem, it being necessary for this purpose to enter into the investigation regarding the colour and luminosity relations before referred to. The quantities $d\mathrm{E}_1$, $d\mathrm{E}_2$, and $d\mathrm{E}_3$ are taken to represent the magnitudes of the differential perceptions for the elementary observations, and $d\mathrm{E}$ is the magnitude of the difference in the colour resulting therefrom. This latter quantity had to be expressed in terms of x, y, and z, and for this purpose the following formula was arrived at (p. 453):—

$$\frac{d\mathrm{E}}{k} = \frac{\delta\lambda}{\sqrt{3}} \sqrt{\left(\frac{1}{x} \cdot \frac{dx}{d\lambda} - \frac{1}{y} \cdot \frac{dy}{d\lambda}\right)^2 + \left(\frac{1}{y} \cdot \frac{dy}{d\lambda} - \frac{1}{2}^{*} \frac{dz}{d\lambda}\right)^2 + \left(\frac{1}{z} \cdot \frac{dz}{d\lambda} - \frac{1}{x} \cdot \frac{dx}{d\lambda}\right)^2},$$

where λ = wave-length, $\delta\lambda$ = a certain mean error, and k a constant found by multiplied observations. This equation has to do with the sensitiveness to colour.

With the aid of the constants, having given an observation of the values of R, G, and V, at any wave-length, the values of x, y, and z may also be found, and the constants must be such that $d\mathrm{E}$, determined by the above equation, shall be equal, or nearly so, at all points of the spectrum.

Having got this constant value of $d\mathrm{E}$, it has then to be compared with the equation for $d\mathrm{E}$ arrived at in a different way, from $d\mathrm{E}_1$, $d\mathrm{E}_2$, and $d\mathrm{E}_3$, viz.

$$d\mathrm{E} = k . \epsilon . \sqrt{3},$$

where ϵ is a certain very small fraction, also arrived at by observation. This second value of $d\mathrm{E}$ has to do with the sensitiveness to luminosity. And if the two values are equal or nearly so, the calculation may be considered justified.

* Probably this is a misprint for $\frac{1}{z}$. The book unfortunately contains several typographical errors.

The most suitable constants were found to be, in round numbers,

$$x = 0{\cdot}80 \,.\, \mathrm{R} - 0{\cdot}35 \,.\, \mathrm{G} + 0{\cdot}55 \,.\, \mathrm{V},$$
$$y = 0{\cdot}26 \,.\, \mathrm{R} + 0{\cdot}35 \,.\, \mathrm{G} + 0{\cdot}39 \,.\, \mathrm{V},$$
$$z = 0{\cdot}25 \,.\, \mathrm{R} + 0{\cdot}125 \,.\, \mathrm{G} + 0{\cdot}625 \,.\, \mathrm{V},$$

where R, G, and V represent the quantities of each elemental colour in a given spectral hue.

To carry out the calculations, an immense number of observations were collected on the various spectral colours (some 50 on each hue), determining the proportions of R, G, and V in each colour. For example: at w.l. 520, the green hue was found to be made up of

$$4{\cdot}62 \text{ of } \mathrm{R} + 8{\cdot}45 \text{ of } \mathrm{G} + 1{\cdot}10 \text{ of } \mathrm{V};$$

then, applying the above equations to these figures, the proportions of the three fundamental colours contained in this hue of the spectrum were found to be

$$1{\cdot}37 \text{ of } x + 4{\cdot}51 \text{ of } y + 2{\cdot}90 \text{ of } z.$$

Or in 100 parts of the green,

$$15 \text{ of } x + 51 \text{ of } y + 34 \text{ of } z.$$

This being done for many points along the spectrum, and the comparisons being satisfactory, the fundamental colours can be laid down in a triangle, and their relations with the spectrum shown in a geometrical form. The results will be found in the tables on pages 454 and 455 and in the diagram on page 457.

The three newly-found fundamental colours are, generally speaking, red, green, and blue; but all very much more highly saturated than anything in the spectrum.

The Red, x, is a highly saturated carmine-red, more tending to blue than the extreme red of the spectrum.

The Green, y, is a yellow-green about w.l. 560, somewhat greener than the complement to violet, and nearly corresponding to the green of vegetation.

The Blue, z, is about w.l. 482, corresponding to ultramarine.

The author states that the fundamental red and blue correspond with Hering's anticipations (*Vermuthungen*); and I may be allowed to say that the former agrees with my determination of my own wanting colour in 1856, before any one suspected the existence of an extra-spectral fundamental.

The following short table, which I have made out from the diagrams, tables, and formulæ, will show, in a simple manner,

the percentages of the "Urfarben," x, y, and z, contained in some of the chief hues of the spectrum.

	Wave-lengths.	x.	y.	z.
Red	end.	61	20	19
Orange	600	47	30	23
Yellow	580	36	39	25
Green	520	15	51	34
Blue	480	31	29	40
Violet	end.	35	25	40
White		33	33	33

If we apply to these quantities the principle that a mixture of equal proportions of the three fundamental colours will make white, we may form an idea of the enormous grade of saturation of the ideal fundamental colours, compared with that of the spectral hues. For example, spectral red will contain 42 parts of x, 1 part of y, and 57 of white; spectral yellow will contain 11 parts of x, 14 of y, and 75 of white; spectral blue will contain 2 parts of x, 11 parts of z, and 87 parts of white. This is a somewhat astounding idea; but a glance at the diagram on page 457 will show it is what the author intends.

The author points out that all simple colours excite the three nerve-elements simultaneously, and with only moderate distinctions of intensity; facts for which there are analogous phenomena in the known photochemical effects of photography.

This brief account gives a very vague idea of the skill and labour that has been embodied in the work referred to; and, considering the entire novelty and difficulty of the attempt, the acuteness of the logical reasoning required, and the complicated nature of the relations involved, I should venture to say it may be pointed to as one of the most striking examples of the application of high mathematics to physiological research.

But it may be asked, What immediate connexion has this with Colour-blindness? The author has himself answered the

question by immediately going on, page 458, to a further investigation, entitled "*Comparison with Dichromic Eyes.*"

He begins with the remark that the fundamental colours he has found do not coincide with those which König and Dieterici had deduced from the comparison of colour-blind eyes with normal ones, and which he had himself quoted in former parts of this work. They had arrived at pretty nearly the same hues of red and blue, but their third fundamental, green, differed materially, and the intensities were very different in all.

Helmholtz takes some pains to explain and comment on this, showing that the discrepancy is due to the attempt made by König and Dieterici to apply the "old" assumption that dichromic vision was simply caused by the absence of one of the fundamental excitements of the trichromic eye. He mentions that this assumption originated with Young, and was, at an earlier period, accepted by most of the adapters of the theory, including himself and Hering, as well as König and Dieterici, and he thereby gives a good defence for their zealous endeavours, but at the same time he leaves no doubt that this assumption has vitiated their results.

As a further proof of this he cites (p. 461) the determination by König and Dieterici of the colours wanting to the red and green blind respectively, according to the fundamental colours chosen by them; and he shows that when the newly found fundamentals are substituted, such a determination leads to irrational results, giving negative values; whereas (p. 460) Young's hypothesis only allows positive values of the physiologically possible colours.

Considering therefore, apparently, the old assumption as now proved intractable, he goes on to explain that a more general hypothesis respecting the existence of dichromatism may be found, in which the necessity ceases that the missing colour should be one of the fundamentals*.

* The following are the original words:—"Die hier gefundenen Grundfarben stimmen nicht mit denen überein, welche die Hrn. A. König und C. Dieterici aus der Vergleichung farbenblinder Augen mit normalsichtigen hergeleitet haben. Nur die besondere, von Th. Young ausgegangene und von den meisten Bearbeitern der Theorie, auch von mir selbst, von E. Hering, A. König, und C. Dieterici früher angenommene Erklärungsweise, dass bei den Dichromaten einfach eine der Grunderregungen des trichromatischen Auges nicht zu Stande komme, tritt in Widerspruch mit dem bezeichneten Ergebniss.

"Aber es ist eine allgemeinere Hypothese über das Wesen der Dichromasie möglich, bei welcher die Nothwendigkeit aufhört, dass die fehlende Farbe eine der Grundfarben sei, und doch die Regel festgehalten wird dass alle Farbenpaare, welche für das normale trichromatische Auge gleich aussehen, auch für das dichromatische gleich aussehend bleiben."

He first shows the possibility of this by a simple example. Suppose, he says, that the rays which ordinarily excite the green sensation do not excite the green sensitive nerves, but do continue to excite the red and blue ones. The eye would become dichromic, and according to the old explanation would see only red and blue. But these two sensations will not be the same as the trichromic red and blue, in which the green element forms part; and further, it is possible that the green nerves, though not excited by the green rays, might retain their former excitability by the red and blue ones,—in which case the dichromic colours would be a certain kind of yellow and blue.

The author then explains (pages 458 to 461) his "*Allgemeinere Form der Dichromasie.*" First, by algebraical reasoning. If x, y, and z represent the three fundamental colour-sensations in the normal eye, and X, Y, Z the three in the dichromic eye, then, as all matches for the former are also good for the latter, X, Y, Z must be linear functions of x, y, z, and the following equations are arrived at, namely :—

$$0 = \alpha X + \beta Y + \gamma Z.$$

$$X = p_1 x + p_2 y + p_3 z.$$

$$Y = q_1 x + q_2 y + q_3 z.$$

$$Z = a X + b Y.$$

The result being that the whole colour value of the dichromic eye appears as a mixture, in variable proportion, of two definite compound colours, X and Y.

Another explanation is given by geometry, in which the author uses a more comprehensive mode than the ordinary plane diagrams. He adopts Lambert's plan of geometry of three dimensions. The values of the three trichromic fundamentals x, y, z, are used as rectangular coordinates, by which may be formed an imaginary parallelopipedon (like a brick whose three dimensions $9 \times 4\frac{1}{2} \times 3$ will represent x, y, and z respectively): then the extreme corner most distant from the origin of the coordinates will represent the place of the compounded colour; the length of the diagonal line drawn between these two points will represent the quantity of the colour, and its direction will represent the hue. Planes may be also drawn intersecting the figure, which will represent the ordinary plane colour-diagrams, and will serve as the bases of "Lambert pyramids," containing all the colours physiologically possible. It is shown that, under the conditions of dichromatism, the resulting planes will each be uniformly

coloured, and the trichromic variety of hues will no longer exist.

This more general theory of dichromatism appears, so far as I can understand it, to amount to the view that while the two dichromic hues must be in some way derived from the three fundamental colours of normal vision, there is no necessary condition as to the manner of their derivation, or as to what they shall be*.

The author, further, in regard to his new theory, calls attention to a point of considerable importance. One of the greatest stones of stumbling for years past has been the division, consequent on the "old" explanation, of dichromic patients into the two theoretically distinct classes of "red-blind" and "green-blind." It is obvious that this division naturally disappears when the old explanation is abandoned; but Helmholtz takes pains to show geometrically that his new theory gives no place for such a division. And he, moreover, expresses the opinion that such a division does not seem to have been fully justified by observation.

He adds, "By this it is also shown that the want of correspondence between the absent colour of the dichromic system and one of the fundamental colours found by us, does not involve any insoluble contradiction †.

It is not my business to offer any comments on the views I have endeavoured (imperfectly I fear) to call attention to; I have only to repeat the reference to the original for fuller information regarding them. But even though there should be differences of opinion on minor points, there can be none as to the character of the work or the position of its author among the great men of the age.

Athenæum Club, S.W., December, 1892.

* Only it would seem that as the dichromic eye now loses nothing, but uses the whole of the three fundamentals and no more, and as their sum makes normal white, then the total sum of the dichromic vision must make normal white also, and the two hues, X and Y, will be complementary.—W. P.

† On account of the great importance of these two expressions of opinion, I subjoin Helmholtz's own words (page 461):—"In unseren Betrachtungen ist keinerlei Beschränkung für die Lage der Schnittpunktes gegeben. Daher fällt bei dieser Verallgemeinerung der Theorie der Dichromasie auch die Trennung in zwei scharf getrennte Klassen, Grünblinde und Rothblinde, weg, welche ja auch den Beobachtungen gegenüber nicht ganz gesichert erscheint.

"Damit ist auch nachgewiesen, dass der Mangel an Ueberstimmung zwischen der fehlenden Farbe der dichromatischen Systeme und je einer der von aus gefundenen Grundfarben keinen unlöslichen Widerspruch einschliesst."

VI. *A New Method of treating Correlated Averages.* *By* Professor F. Y. Edgeworth, *M.A.*, *D.C.L.**

THE following is a simpler method of solving one of the problems treated in a former paper relating to *correlated averages*†. Taking the case of three variables for convenience of enunciation, let us put for the exponent (of the expression for the probability that any particular values of the variables will be associated)

$$R = ax^2 + by^2 + cz^2 + 2fyz + 2gxz + 2hxy.$$

And let it be required to determine the coefficients a, b, c, &c.

The most probable values of y and z corresponding to any assigned value of x, say x', are deduced from the equations

$$\begin{cases} by + fz + hx' = 0, \\ cz + fy + gx' = 0. \end{cases}$$

The values of y and z determined from these equations may indeed diverge widely from the particular values corresponding in any one specimen to x'. But if we take a number of specimens, it becomes more true‡ that

$$\begin{cases} bSy + fSz + h\Sigma x' = 0, \\ cSz + fSy + g\Sigma x' = 0. \end{cases}$$

Dividing each equation by the sum of the assigned values $\Sigma x'$, we have

$$\begin{cases} h\rho_{12} + f\rho_{13} + h = 0, \\ c\rho_{13} + f\rho_{12} + g = 0\ ; \end{cases}$$

where ρ_{12}, ρ_{13} mean (as in the former paper) the coefficients of correlation pertaining to each couple of organs (Mr. Galton's r).

By similarly *assigning* values of y and of z, and *observing* the associated values of the other variables, we obtain six (in general $n(n-1)$) equations for the sought coefficients $a, b, \ldots g, h$; which, being rearranged, are as follows :—

$$\left.\begin{aligned} \rho_{12}a + \rho_{23}g + \quad h &= 0, \\ \rho_{31}a + \quad g + \rho_{23}h &= 0\ ; \end{aligned}\right\}$$

$$\left.\begin{aligned} \rho_{23}b + \quad f + \rho_{31}h &= 0, \\ \rho_{12}b + \rho_{31}f + \quad h &= 0; \end{aligned}\right\}$$

$$\left.\begin{aligned} \rho_{31}c + \rho_{12}f + \quad g &= 0, \\ \rho_{23}c + \quad f + \rho_{12}g &= 0. \end{aligned}\right\}$$

* Communicated by the Author.

† Phil. Mag. August 1892.

‡ Cf. *loc. cit.* p. 191 *et seq.*

A solution of this system is afforded by putting a, b, c each proportional to one of the principal minors, and f, g, h each to a certain one of the other three minors, of the following determinant :—

$$\begin{vmatrix} 1, & \rho_{12}, & \rho_{31}. \\ \rho_{12}, & 1 & \rho_{23}, \\ \rho_{31}, & \rho_{23}, & 1, \end{vmatrix}$$

For call the three minors formed by omitting successively each constituent in the first row a, h, g. By a well-known theorem*, if each of these minors is multiplied by the corresponding constituent in the rows other than the first, the sum of these products $=0$.

That is
$$\left.\begin{aligned} \rho_{12}\mathrm{a}+\mathrm{h}+\rho_{23}\mathrm{g}=0 \\ \rho_{31}\mathrm{a}+\rho_{23}\mathrm{h}+\mathrm{g}=0 \end{aligned}\right\}.$$

Thus the first two of the above-written six equations are satisfied. By parity of reasoning, if we put, for b, the principal minor b, for c, c, and, for f, the minor f, obtained by omitting the row and column containing (either) ρ_{23}, the remaining four equations are satisfied. The proposed system of proportional values is therefore *a* solution. And since the equations are simple, it is *the* solution.

We have thus obtained by a simpler method than before the solution of the problem†: given the values of some of the variables, what are the most probable values of the other variables? For the *proportionate* values of the coefficients $a, b, \ldots g, h$ having been ascertained, we have only to substitute in R the given values of one or more variables, *e. g.* z'; and for the most probable values of the remaining variables we have the equations

$$\left(\frac{d\mathrm{R}}{dx}\right)_{z=z'}=0\,;\quad \left(\frac{d\mathrm{R}}{dy}\right)_{z=z'}=0.$$

But we have not obtained a solution of the second problem‡: given the values of some of the variables, what is the law of dispersion for the remaining ones? For in order to solve this problem we require the *absolute* values of the coefficients. I do not see how to obtain these, except by the method before adopted, viz., obtaining the integrals of the expression

$$\mathrm{J}e^{-(ax^2+by^2+cz^2+2fyz+2gxz+2hxy)}$$

with respect to all but two, and all but one, of the variables.

Balliol College, Oxford.

* Salmon, 'Higher Algebra,' lesson iv. article 27.

† Generalizing the statement given in the former paper, p. 190.

‡ Generalizing the statement given in the former paper, p. 190.

VII. *A necessary Modification of* Ohm's *Law.* *By* Fernando Sanford *.

[Plate III.]

DURING the past year I have been engaged in some investigations which seem to call in question the validity of Ohm's law, by showing that the resistance of a metallic conductor varies with the nature of the dielectric in its field of force. For the purpose of determining if this be the case, I have made a large number of measurements of the resistance of a copper wire in various dielectrics, and have found that in several cases the change of resistance, both in liquid and gaseous dielectrics, is very marked.

The apparatus used consists of a copper tube about four feet long and one inch in internal diameter, closed with copper plates at the end, and having a copper wire 1 millim. in diameter stretched through its centre and fastened by means of a binding-screw to the centre of one end plate, while it passes through an insulating-plug in the centre of the other end plate. The tube is provided with stopcocks at the ends for filling and emptying, and with an opening in the side for inserting a thermometer. The current, which was always between the extremes of five and eight milliamperes, was passed one way through the tube and back through the wire, so that the whole dielectric in its field could be changed at will. The measurements were made by means of a Wheatstone's bridge with arms of 1 : 1000, and a sensitive galvanometer. A change of resistance of 0·1 ohm in the box, which corresponded to ·0001 ohm in the tube and wire, produced a very noticeable deflexion of the galvanometer-needle. The measurements were accordingly estimated with a fair degree of accuracy to ·00001 ohm.

The resistance of the tube and wire was measured in air at different temperatures through a range of about ten degrees Centigrade, and a curve was plotted, using the temperatures as abscissæ and the resistances as ordinates. This curve did not depart appreciably from a straight line. The dielectric to be tested was then poured into the tube, a set of measurements was made in it through the same range of temperatures, the dielectric drawn out, the tube cleaned and dried, and a new set of measurements made in air. This was repeated several times, until it was certain that after each change of dielectrics the resistance returned to the same value which it had previously shown in the same dielectric. In the case of air and petroleum this comparison was carried on for a month, the dielectrics in the meantime being changed five times, and

* Communicated by the Author.

the apparatus being allowed to stand untouched for two weeks to make sure that none of the constants were changing, and in the whole series not a single measurement in either dielectric fell upon or beyond the curve made for the other dielectric (see Pl. III. fig. 1). The resistance of the wire in petroleum was shown to be about ·00006 ohm less than in air; and as the whole resistance of the tube and wire averaged about ·0335 ohm, this difference corresponded to about ·18 of one per cent. of the whole resistance.

Regarding the conductivity of the wire in air as unity, its conductivity in the liquid dielectrics tested was as follows:—

Petroleum	1·0018
Mixture of carbon bisulphide and turpentine	1·0009
Carbon bisulphide, uncertain, apparently	1+
Wood alcohol	·9998
Benzine	·9994
Wood alcohol and benzine	·9985
Absolute alcohol	·9981
Wood alcohol and petroleum	·9973
Distilled water, uncertain, apparently	1−

It will be seen that when two dielectrics which do not seem to mix with each other were used together the resistance of the wire was greatly increased, as in the case of wood alcohol and benzine, and wood alcohol and petroleum. That these liquids do diffuse into each other was shown by measuring the index of refraction of the two components before and after they had stood in contact with each other, and in every case a change was observed.

A similar change of resistance was noticed when the tube contained different gaseous dielectrics. This was first observed when the burning gas used in the laboratory was allowed to enter the tube. This gas was made from gasoline by a machine on the ground, and consisted of the vapour of gasoline mixed with air. A series of measurements was made in this gas and in air, the measurements in air being made both before and after those made in the gas. Of the seventeen measurements with the wire in the gas, only one was as much as ·00001 ohm from the curve drawn, while the nearest distance of any gas measurement to the air-curve was ·00004 ohm, and the average distance of the gas points from the air-curve was ·000058 ohm. From these measurements the resistance of the wire in gasoline burning gas was 1·0017 times its resistance in air (see fig. 2).

The other vapours used were those of volatile liquids, a small quantity of the liquid being poured into the tube and allowed to evaporate. Taking, as before, the conductivity of

the wire in air as unity, the conductivities in the vapours tested were approximately as follows :—

Alcohol vapour	·99949
Chloroform vapour	·99830
Gasoline burning gas	·99820
Sulphuric ether vapour	·99750
Carbon bisulphide vapour, approximately . .	1
Rarefied air, less than	1

Some of the phenomena observed made it seem probable that only that part of the dielectric in direct contact with the wire was concerned in this change of resistance. For example, when the petroleum was poured out of the tube and a measurement made before it had drained off and evaporated, the resistance observed was the same as when the tube was filled with petroleum, and it was only after the tube had been carefully drained out and dried that the resistance returned to its former value in air. In the case of sulphuric ether vapour this phenomenon was very marked. It was only after the tube had been washed out with alcohol one or more times, and had been dried out by drawing a current of air through it for several hours, that the resistance returned to its former value.

I am now engaged in investigating the same phenomenon, using a silver wire of the same size as the copper wire used in last year's experiments. In general, the difference in resistance with the dielectrics above mentioned is less marked than in the case of the copper wire formerly used, but it is still noticeable. As in the case of the copper wire, the greatest variation yet noticed was when the tube was filled with sulphuric ether vapour, but with the silver wire the resistance is decreased in the ether vapour, while with the copper wire it was increased. The same difficulty in removing the effect of the ether vapour also appears with the silver wire, in which case it was only after repeated washings with alcohol that the resistance of the wire returned to its former value.

I have thus far been unable to find with what other properties of the dielectrics these phenomena are correlated, but it seems clear that hereafter Ohm's Law will have to be so modified as to take account of the dielectric surrounding a conductor, as well as the nature and temperature of the conductor itself.

The measurements upon which the above conclusions are based are given in full in a paper entitled "Some Observations upon the Conductivity of a Copper Wire in various Dielectrics," which is now being published by the Leland Stanford Jr. University.

Palo Alto, California,
October 26, 1892.

VIII. *Experiments in Electric and Magnetic Fields, Constant and Varying.* *By* Messrs. Rimington *and* Wythe Smith.*

[Plate IV.]

THE object the authors have in bringing these phenomena before the Society is not to establish any new theory, nor to show imperfections in present theories, but to exhibit experiments which help the actions taking place in a dielectric under stress to be more easily grasped.

The experiments are divided into two sets :—

(1) Performed in electric fields.
(2) Performed in varying magnetic fields.

Although these two fields cannot exist separately, their effects are isolated.

Set 1. *Constant Electric Field.*

A constant electric field was produced by two charged metal disks + and —, each of which was stuck on the outside of a glass plate (Plate IV. fig. 1). The object of the glass plates was to prevent brush discharges between objects placed in the field and the plates.

Fig. 1, *a*, *b* represents a partially exhausted electrodeless tube, placed in the uniform electric field. In the position shown, the tube is at a uniform potential. Now let it rotate in the direction of the arrow ; the potential of *a* will fall and that of *b* rise until the P.D. between the ends is sufficient to break down the tube. There will then be a convection-current equalizing the potential, during the continuance of which the tube will glow. On rotating still further a similar action will take place.

The effect of these actions is to produce a double fan-shaped set of images, as shown in fig. 2. The number of images in the fan depends on the intensity of the field.

This phenomenon is intensified by constricting the middle part of the tube.

In designing the tubes for these experiments, care was taken to have the point where they were connected to the pump in such a position that there was no tendency for discharge to take place at these points when in use. The tubes used in this experiment are shown in fig. 3 (*a*, *b*, *c*, and *d*). The stem was used to connect them to the whirling motor.

The surfaces of these tubes should be fairly clean and dry, and it is advisable with a new tube, or one left unused for some time, to excite it between the knobs of an influence-machine.

In the double fan-shaped set of images (see fig. 4, *a*) one

* Communicated by the Physical Society : read November 25, 1892.

end will be seen to be brighter than the other, the current passing from the dull end to the bright end.

Not only is this effect visible with a straight tube, but on rotating an exhausted bulb in the field a stationary luminous region will be seen (see fig. 4, *b*).

Varying Electric Field.

Instead of rotating the tube a similar effect is produced by varying the field in which the tube is placed.

The tube should be placed with its longer axis in the direction of the lines of force. The plates in this case may either be charged and discharged by an influence-machine and dischargers, the latter sparking, or by an induction-coil, with or without sparking.

When an induction-coil is used, very long tubes will glow when brought near.

Set 2. *Magnetic Field.*

The authors were of the opinion that, by taking advantage of the action of the Geissler tube, one might show Hertzian phenomena to fairly large audiences. They therefore substituted a Geissler tube for the spark-gap in the resonator.

This was very successful with a Leyden-jar oscillator (fig. 5). The oscillator and resonator consisted of two similar small Leyden jars for capacity, and a single convolution of thick copper wire for the conductor-circuit. The Geissler tube was placed as a shunt to part of the conductor-circuit of the resonator (see fig. 5).

But although they designed special tubes, they were unable to get good results with the ordinary forms of Hertz oscillator and resonator.

They next made a resonator of the following form:—

Two metal plates, *a* and *b* (fig. 6), give capacity, and the wire self-induction. An electrodeless exhausted tube was placed as dielectric between the plates. When a fairly large Hertz oscillator was used, this tube glowed brightly, even when taken to considerable distances.

Glow produced in varying Magnetic Fields.

Instead of, as in the last set of experiments, having a secondary composed partly of a metallic conductor and partly of a vacuum-tube, the whole circuit may be composed of rarefied gas. It is evident that, in order to generate a current in such a circuit, a large induced E.M.F. would be required; this would necessitate either a very strong magnetic field, or one which changed very rapidly. The former was out of the question, the latter was obtained by taking advantage of

the phenomenon of oscillatory discharge in the following manner :—

P (fig. 7), a primary consisting of a very few turns of gutta-percha covered wire, was placed in a Leyden-jar circuit, as shown. As a secondary an exhausted bulb, or annular tube, was placed near P.

On sparks passing at D, a bright ring of light appeared in the secondary.

In the actual experiments a metallic secondary, S, was also wound with P and exactly similar to it. On short-circuiting S, the induced current in this circuit will weaken the magnetic field so as to completely extinguish the Geissler secondary.

If S is connected to a third coil this coil will behave in a similar manner to P, with weaker effects; P and S in this case form a one to one transformer.

The wire of the coil P is itself luminous when S is open; short-circuiting S will stop this effect.

(Since the authors started their researches some of these latter experiments have been shown by Prof. Thomson.)

Appendix.

Theory of a Vacuum-tube in a varying Electric Field.

When an electrodeless vacuum-tube is placed axially between two plates, and a potential difference established between them, the tube forms part of the dielectric between the plates, and some of the lines of induction pass through the tube. Now a rarefied gas is a very weak dielectric, and readily gives way under the electric stress; a convection-current flowing through the tube (during which time the gas in the tube behaves as if it were a conductor)*.

This results in the ends† of the tube becoming charged, or lines of induction from the plates terminate on the ends of the tube, there being no lines in the tube itself (see fig. 8). The whole of the tube will also be at the same potential.

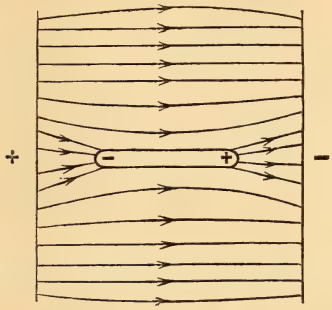
When the plates are discharged, the lines of induction passing from the plates to the ends of the tube will now pass through the tube; the rarefied gas will again break down under the electric stress, and a convection-current will pass

* Of course the tube will not conduct after the manner of a copper wire, but rather like a quantity of pith balls between two conducting plates.

† By the term "ends" is meant the *inside* surface of the glass at the ends of the tube.

through the tube until the charges at the ends neutralize each other.

Fig. 8.



If the change in the electric field take place rapidly enough, the convection-current will produce sufficient disturbance of the molecules to cause luminosity.

Theory of a Vacuum-tube rotating in a constant Electric Field.

Consider the tube in a constant field in position $a\,b$ (fig. 9). There will be a — charge at "a" and a + one at "b", and the tube will behave as a nonconductor. We shall in fact have conditions similar to those in fig. 10, where "c" and

Fig. 9.

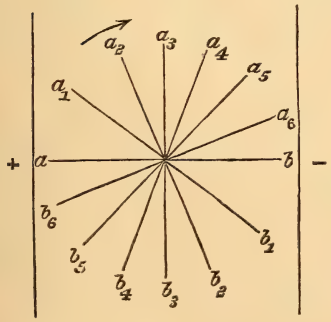
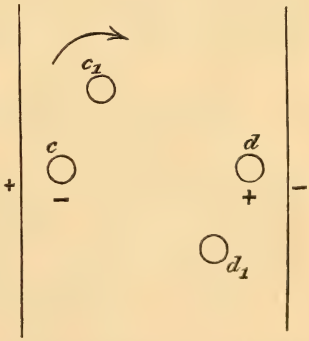


Fig. 10.



"d" are two insulated conductors, which have been previously connected together by a conductor, and which correspond to the ends of the tube.

Imagine now "c" and "d" to be moved to positions c_1 and d_1; they will now be no longer at the same potential, and, if connected together, a current will flow from d_1 to c_1, again equalizing their potentials.

The same will happen to the tube if it move during rotation from position $a\,b$ to $a_1\,b_1$; and, when the potential difference between its ends attains a sufficient magnitude, the dielectric of rarefied gas will break down, a convection-current flow from b_1 to a_1, and the tube for the instant will behave like a conductor. During this instant of breaking down the tube will glow. After this the tube will behave like a nonconductor, the ends being at the same potential until the tube rotating moves into position $a_2\,b_2$, and, if the potential difference between a_2 and a_1 is equal to that between a and a_1, and the same for the b's, the tube will glow for an instant at position $a_2\,b_2$.

In the same way it will glow in the positions $a_3\,b_3$, $a_4\,b_4$, &c., if continuously rotated in the direction of the arrow. The points $a_3\,a_4$ &c., $b_3\,b_4$ &c. are such that the potential difference between each consecutive two is approximately the same. As the glow takes place at the end of each alteration of the potential difference, it is obvious that the double fan-like set of images obtained will not be symmetrical with respect to the plates, but will be displaced in the direction of rotation by about one image.

The number of images in a single revolution will be proportional to the potential difference between the plates, but will not depend on the speed of rotation, provided that speed exceed a certain limit. The effect of increasing the speed is, however, to apparently increase the number of images; since those of one revolution do not fall in exactly the same positions as those of the preceding one, and the images of several revolutions are seen simultaneously on account of persistence of vision.

Discharge through Coil surrounding exhausted Bulb.

When a Leyden jar is discharged through a coil of wire, the varying magnetic induction due to the discharge-current will cause an E.M.F. to act in the dielectric inside and outside the ring in a series of concentric circles. Let r be the radius of the coil: consider a circular path in the dielectric of radius x less than r. If the magnetic induction passing through the coil were uniformly distributed, the number of lines passing through the path x would be proportional to its area or to x^2, and the E.M.F. per unit of length along it to x^2 divided by its circumference or to $\frac{x^2}{x}$, *i. e.* to x. Hence the electric stress along a circular path x in the dielectric is greater the larger x. Of course the actual distribution of the magnetic induction is not uniform, but increases as we pass from the centre to the

circumference: this will of course make the electric stress increase more rapidly than x. When the dielectric is a rarefied gas it is not broken down until the electric stress exceeds a certain value: hence the discharge takes the form of a luminous ring in the outside of the bulb. By increasing the sparking-distance in discharging the Leyden jar the magnetic induction is increased, making the electric stress greater and broadening the ring.

The breadth of the ring also depends on the degree of exhaustion of the bulb, as the value of the electric stress requisite to break down the rarefied gas depends on the degree of rarefaction. In the case of an annular exhausted tube placed outside the coil the luminous ring will be nearest to the inner side of the tube: since when x is greater than r, the E.M.F. per unit of length is less the greater x, on account of the lines of magnetic induction outside the coil being in the opposite direction through the path x to those inside the coil.

IX. *Notices respecting New Books.*

Odorographia: a Natural History of Raw Materials and Drugs used in the Perfume Industry. By J. C. Sawer, *F.L.S.* London: Gurney and Jackson. 1892.

IN this work by Mr. Sawer we have another illustration of the intimate relation existing between science and industry which is such a striking feature in the educational movement of the time. No book has yet appeared in which the ground covered by the present author has been traversed by any writer who has brought such qualifications to bear upon the subject, and we have as a result a volume which may fairly be commended as unique in its way, and which will prove a boon to all interested in the chemistry, natural history, and technology of the numerous materials used in perfumery.

A very brief description of the contents will suffice to show how thoroughly the subject has been handled. In the first chapter, devoted to musk, we have an account of civet and ambergris, and a list of all the animals and plants which give this odour, together with a description of the artificial musk recently introduced by Baur, and obtained by the nitration of certain coal-tar hydrocarbon derivatives. The second chapter, on the odour of roses, is a very long one, and deals first with the true "otto of rose" manufactured in Bulgaria and elsewhere, the chemistry and technology of which are given in considerable detail, and illustrated by figures of the apparatus used and a map of the Bulgarian rose-farm district. An account of rose culture in France is also given, and a description of other odoriferous substances resembling rose, such as pelargonium, and artificial rose perfumes, such as ammonium salicylate,

methylbenzylenic ether, phenyl paratoluate, citronellic aldehyde, &c. The actual methods of extracting the oil of rose by maceration, enfleurage, and by the use of various solvents, are fully discussed and illustrated by figures. The "citrine odours" are described in the third chapter. These comprise the oils of orange, lemon, lime, shaddock, and bergamot; incidentally sylvestrine is referred to, and the oils of neroli, citronella, and lemon-grass (*Andropogon citratus*, DeCand.) receive adequate consideration. Jasmine, jonquil, and hyacinth are treated of in the fourth chapter, the odour of violet in the fifth, ylangylang &c. in the sixth, and the "odour of the hayfields" in the seventh. In this last chapter we find an account of coumarin, both natural and synthetical. The eighth chapter, on vanilla, claims over 30 pages, and is remarkably complete from every point of view. In the ninth chapter the bitter almond, cherry laurel, and heliotrope are treated of; in the tenth chapter, cinnamon, cassia, and clove; in the eleventh, benzoin, storax, and the balsams; and in the twelfth, opoponax, bdellum, myrrh, &c. Lign-aloes, patchouli, and related perfumes are described in the thirteenth chapter; santal and cedar in the fourteenth; camphor in the fifteenth; cajeput, lavender, and rosemary in the sixteenth and concluding chapter.

There can be no doubt, from this epitome, that Mr. Sawer has succeeded in carrying out the idea set forth in the preface, wherein he states:—"An endeavour has here been made to collect together into one Manual the information which has hitherto been only obtainable by reference to an immense number of works and journals, English and foreign, in many cases inaccessible to readers interested in the subject."

It is not only as a technical work, however, that the present volume demands notice in this Magazine. Although professedly addressed to technologists, its subject-matter appeals both to botanists and chemists; and the latter will be surprised to find what a large and interesting field of work is before them for investigating the constitution of the numerous odorous compounds furnished by the vegetable kingdom or synthesized in the laboratory and factory. New outlets for tar-products may be looked for in the direction of the perfume industry; and in bringing together all that is known in connexion with the subject, Mr. Sawer has done good service to a somewhat neglected branch of applied science.

X. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxiv. p. 385.]

November 9th, 1892.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

THE following communications were read:—

1. "A Sketch of the Geology of the Iron, Gold, and Copper Districts of Michigan." By Prof. M. E. Wadsworth, Ph.D., A.M., F.G.S.

After an enumeration of the divisions of the Azoic and Palæozoic

systems of the Upper and Lower Peninsulas of Michigan, the author describes the mechanically and chemically formed Azoic rocks, and those produced by igneous agency, adding a table which shows his scheme of classification of rocks, and explaining it.

The divisions of the Azoic system are then described in order, beginning with the oldest—the Cascade Formation, which consists of gneissose granites or gneisses, basic eruptives and schists, jaspilites and associated iron ores, and granites.

The rocks of the succeeding Republic formation are given as nearly as possible in the order of their ages, commencing with the oldest:—Conglomerate, breccia and conglomeratic schist, quartzite, dolomite, jaspilite and associated iron ores, argillite and schist, granite and felsite, diabase, diorite and porodite, and porphyrite. The author gives a full account of the character, composition, and mode of occurrence of jaspilite, and discusses the origin of this rock and its associated ores, which he at one time considered eruptive; but new evidence discovered by the State Survey and the United States Survey leads him to believe that he will have to abandon that view entirely.

In the newest Azoic formation, the Holyoke formation, the following rocks are met with:—Conglomerate, breccia and conglomeratic schist, quartzite, dolomite, argillite, greywacke and schist, granite and felsite (?), diabase, diorite, porodite, peridotite, serpentine, and melaphyre or picrite. The conglomerates of the Holyoke formation contain numerous pebbles of the jaspilites of the underlying Republic formation; a description of the Holyoke rocks is given, and special points in connexion with them are discussed.

The author next treats of the chemical deposits of the Azoic system, gives a provisional scheme of classification of ores, and discusses the origin of ore deposits.

The rocks of the Palæozoic system are next described, and it is maintained that the eastern sandstone of Lower Silurian age underlies the copper-bearing or Keweenawan rocks. The veins and copper deposits are described in detail, and the paper concludes with some miscellaneous analyses and descriptions, as well as a list of minerals found in Michigan.

2. "The Gold-quartz Deposits of Pahang (Malay Peninsula)." By H. M. Becher, Esq., F.G.S.

The gold-quartz deposits of Pahang traverse an extensive series of slates, sandstones, and dark-coloured limestones, sometimes more or less metamorphosed, and probably of Palæozoic age, occupying the low-lying hill-country on the eastern side of the central granitic mountain-range. The prevailing dip of the strata is eastward.

In some places the auriferous rock penetrates adjacent intrusive syenites, but has not been traced in connexion with the main granitic 'massif' which is generally considered to be the matrix of the cassiterite found in the 'Straits' alluvial Tin-fields.

The gold occurs in lodes and irregular formations, which, however, are not distinguished from one another by any hard-and-fast

line; the difference depends on the size, shape, and continuity of the quartz veins, though even the lodes seldom maintain their regularity for more than a few score feet. The quartz often occurs in very narrow veins intersecting one another to form what may be called 'stockworks.' It is probably from these minute veins that the alluvial gold is derived. In the Raub mine numerous rich veinlets occur in a certain zone where the whole slate-rock is charged with iron pyrites, probably auriferous. Many 'stockworks' are intimately associated with dykes or intrusions of a rock which may be called trachyte-porphyry, and these igneous rocks are decomposed where prominently associated with auriferous quartz.

3. "The Pambula Gold-deposits." By F. D. Power, Esq., F.G.S.

The Pambula Gold-field is situated in the parish of Yowaka, County of Auckland, in the South-eastern corner of New South Wales.

The lodes are different from ordinary auriferous deposits, inasmuch as the material filling the ore-channels does not differ greatly in appearance from the 'country' rock, and is but slightly mineralized. The 'country' rock is 'pyrophyllite schist,' associated with 'felspar-porphyry,' sometimes turning into 'quartz-porphyry,' the whole being tilted at a high angle. The bedding and cleavage-planes appear to be coincident. The rock forms lenticles both microscopic and macroscopic. Some of the lodes are accompanied by a quartz 'indicator' which contains little or no gold in itself, the precious metal being found in the shattered 'country' rock of its footwall. On the footwall-side this shattered zone gradually merges into the ordinary 'country' rock. The cause of the parallelism of the auriferous lodes, the mountain-ranges, and the seacoast is discussed, and it is pointed out that the gold does not occur in large grains.

XI. *Intelligence and Miscellaneous Articles.*

AN ELECTROLYTIC THEORY OF DIELECTRICS.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

SINCE writing the paper on dielectrics which you published in your last issue, it has occurred to me that the calculation of q from tenacity and dielectric strength might be made directly, instead of in terms of specific inductive capacity and Young's modulus. Perhaps it may be well to point this out.

Disruptive discharge occurs when the mechanical force on a molecule is equal to $\frac{T}{n} = Td^2$; and as the force applied electrically is equal to $q \times \frac{dV_{max.}}{ds}$, it follows that

$$q\frac{dV_{max.}}{ds} = Td^2.$$

From this q for glass $= \frac{1}{2} \times 10^{-11}$—a number which is probably

rather too small, for two reasons: firstly, because flaws reduce T more than $\frac{dV_{max.}}{ds}$ (as I explained in the paper); and, secondly, because the measured value of T depends on the cohesion between the least-paired particles, whereas $\frac{dV_{max.}}{ds}$ depends on that between those which are most paired.

With liquids the second of these causes of error will be more marked than with solids, because the pairing in them is so much more pronounced; so that although the measured values of T for liquids are probably much lower than for solids, the true values for electrical stress are likely to be the same for both, or even higher for liquids. It is therefore significant that $\frac{dV_{max.}}{ds}$ is so nearly the same in the three substances, glass, water, and oil, for which I measured it; for constancy in the values of q and T involves, of course, constancy in the values of $\frac{dV_{max.}}{ds}$ (to within the limits of variation of d).

I am, Gentlemen,

University College, Bristol, December 15, 1892.

Your obedient servant,

A. P. CHATTOCK.

ON A CHEMICAL ACTINOMETER. BY H. RIGOLLOT.

This apparatus consists of two plates of oxidized copper immersed in water containing $\frac{1}{1000}$ of chloride, iodide, or bromide of sodium. One of the plates is exposed to the rays of light, the other is protected from the action either by surrounding it with parchment or paper, or by placing it directly behind the first plate at a distance of about a millimetre.

The action of the light is instantaneous and disappears when the illumination is destroyed.

The sensitiveness of an element decreases rapidly at first and then becomes virtually constant.

The electromotive force of a given actinometer varies with the colour of the light which acts upon it.

M. Rigollot has investigated the electromotive force in the different parts of the spectrum, and gives the curves obtained by taking as abscissæ the lengths of waves, and as ordinates the divisions read off on the galvanometer-scale. These curves show that the actinometer with copper plates is most sensitive in the red portion of the spectrum, that is in the region most luminous for the eye. In this respect it differs from actinometers with silver compounds, which are more especially sensitive to the most refrangible rays.

If, after having traversed the spectrum from red to violet, the system of plates is again exposed in all parts of the spectrum but proceeding from violet to red, the curves retain the same form, and the increase of sensitiveness for red rays observed by M. Becquerel (*Lumière*, vol. ii. page 138) for iodized plates which

have been previously exposed to the most refrangible rays, does not seem here to take place.

M. Rigollot used his actinometer to investigate the light diffused by the northern region of the sky at different times of the day. He gives the curve obtained on September 17, 1889, on the terrace of the Physical Laboratory of the Faculty of Science at Lyons with a clear sky. This shows a maximum illumination towards half-past twelve; the curve is virtually symmetrical with respect to this maximum for different times of day.

The author has investigated if, as M. Egoroff has found for iodized plates, the intensity of the current is inversely proportional to the square of the distance from the source to the apparatus. This law holds approximately with Drummond's light as source, that is to say with a feeble light, but with sunlight the intensity increases more rapidly than the intensity of the current.

As the indications of the instrument are proportional to the illumination for faint light, it may be used with advantage in certain cases, such as examining the luminosity of the sky in diffused light.—*Journal de Physique*, November 1892; from *Annales de Chimie et Physique*, vol. xxii. p. 567, 1891.

ON THE ATTRACTION OF TWO PLATES SEPARATED BY A DIELECTRIC. BY M. JULIEN LEFEVRE.

I have measured the attraction of two electrified plates separated by a dielectric not in close contact with them, and have verified that it is represented by the following formula:—

$$\frac{F}{F'}=\left(\frac{e+e'}{\frac{e}{k}+e'}\right)^2;$$

where F′ is the attraction of the two plates at the distance $e+e'$ in air; F the attraction at the same distance when a plane insulating plate of thickness e has been placed between the plates; e' is then the sum of the thicknesses of air on either side of this plate; k is the dielectric constant of the plate.

I used two horizontal plates, and a sensitive balance to the beam of which was hung at one end a scale-pan; the movable plate of the electrical apparatus, which is 12 centim. in diameter, is suspended at the other end by an insulating stem. This plate is surrounded by a guard-ring provided with a kind of cover, which is only perforated by a hole to allow the rod to pass.

The fixed plate, which is 19 centim. in diameter, is placed below the former and rests on an insulating support with levelling-screws, so that the distance $e+e'$ can be varied. Three insulating rods pass through this plate and support the dielectric. On either side of this are layers of air as thin as possible; it must, however, be possible for the movable plate to make small oscillations.

The source of electricity is a Ruhmkorff's coil worked by six Bunsen's elements. One of the poles communicates with the fixed plate, and with the inner coating of a jar the capacity of

which is, according to circumstances, 70 to 150 times greater than that of the condenser formed by the two plates. The other pole, the external armature of the jar, the movable plate, and the beam of the balance are put to earth.

The whole apparatus except the scale-pan is placed in a cage the air of which is dried.

The plates of sulphur and of paraffin are obtained by melting in a mould, the bottom of which is carefully levelled. The thickness of the plate is measured by a two-ended screw and a cathetometer. The distance between the two plates is also measured by a cathetometer.

The dielectric is placed in the cage some days before the experiment so as to get rid of all traces of electricity.

The balance being somewhat too lightly tared, and all parts being put to earth, I counterpoise by a weight p. I then electrify the fixed plate, and counterbalance again with a weight P. I put this plate to earth and counterpoise again by a weight p': then

$$F=P-\frac{p+p'}{2}.$$

The attraction F′ is determined in like manner by three operations.

I work in the same way with liquids, measuring F′ first, and then F so as to avoid evaporation. The thickness of air e' undergoes in this case a slight correction, which consists in replacing the thickness of the layer of air forming the bottom of the vessel containing the liquid by the equivalent thickness of air.

In each experiment I calculate the ratio $\frac{F}{F'}$, and then the corrected ratio

$$R=\frac{F}{F'}\left(\frac{e+ke'}{e+e'}\right)^2.$$

From (1) we should have $\sqrt{R}=k.$

The following table, in which e and e' are expressed in centimetres, F and F′ in milligrammes, shows that the values of $\sqrt{R}$ agree with the values of k which I have obtained by means of Coulomb's balance (*Comptes Rendus*, Nov. 16, 1891).

The formula (1) is therefore correct; and particularly in the case in which e' can be disregarded, we have $\frac{F}{F'}=k^2$.

Dielectric.	e.	e'.	F.	F′.	$\frac{F}{F'}$.	R.	$\sqrt{R}$.	k.
Paraffin, No. 1	2·20	0·70	39·5	17·25	2·29	3·53	1·88	2
" "	"	0·66	40·5	14	2·89	4·38	2·09	"
" No. 2.....	3·37	0·61	30·5	9	3·39	4·51	2·12	"
" "	"	0·68	23·5	7·25	3·24	4·42	2·10	"
Sulphur	3·56	0·54	48·5	9·75	4·97	7·27	2·70	2·6
Ebonite	2·04	0·32	72·75	18·75	3·88	5·39	2·32	2·3
Carbon bisulphide...	2·60	1·09	22	11·5	1·91	2·78	1·67	1·7
Oil of turpentine ...	2·77	0·79	26·25	13	2·02	2·49	1·58	1·5
Petroleum	2·28	0·71	19·50	8	2·43	3·38	1·84	1·9

I may, in conclusion, observe that the attraction of two plates lends itself perfectly to the measurement of dielectric constants; it is simple, rapid, and only requires a sensitive balance, and is preferable to all methods now in use.—*Journal de Physique,* June 1892.

INVESTIGATION OF THE PROPERTIES OF AMORPHOUS BORON.

BY H. MOISSAN.

Pure amorphous boron, obtained by reducing boric anhydride by means of magnesium, is a bright chestnut-brown dirty powder, of specific gravity 2·45. Even in the electric arc it cannot be melted; heated for a long time to 1500° it agglomerates, but not to any great extent. The electrical conductivity is small; the specific resistance $\alpha = 801$ megohms.

Heated in the air, amorphous boron takes fire at 700°, and burns with production of sparks. It burns in oxygen with a brilliant lustre; with sulphur also it unites at 610°, with incandescence, boron sulphide being formed. Boron takes fire in chlorine at 410°; it burns with bright incandescence, forming chloride; bromine acts in an analogous manner.

Amorphous boron combines with metalloids more readily than with metals. At a high temperature it combines, however, with magnesium, iron, and aluminium, and more readily still with silver and platinum.

Very concentrated nitric acid readily acts on amorphous boron and with ignition. Sulphuric acid is reduced to sulphurous; phosphorus is separated from phosphoric acid at 800°, arsenic from arsenic acid, and iodine from iodic acid.

Boron is a powerful reducing agent, exceeding carbon and silicon in this respect, for at a red heat it can withdraw oxygen from carbonic oxide and from silica. It can readily reduce a number of metallic oxides; CuO, SnO, PbO, SbO_3, and Bi_2O_3, even on moderate heating, part with their oxygen to boron, with incandescence. Lead peroxide detonates violently when rubbed with boron in a mortar; and a mixture of sulphur, nitre, and boron detonates under a red heat like gunpowder.

Amorphous boron also has a reducing action on a great number of salts; the sulphates of potassium and sodium, as well as those of calcium and barium, are reduced by boron to sulphides as by carbon. Silver is separated in beautiful crystals from solutions of silver nitrate; and from solutions of palladium, platinum, and gold the corresponding metals.

Boron unites directly with nitrogen only at very high temperatures.

Amorphous boron shows thus in its chemical relations remarkable analogies with carbon.—*Comptes Rendus,* vol. cxiv. p. 607.

THE

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AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

FEBRUARY 1893.

XII. *The Diffusion of Light.* *By* W. E. SUMPNER, *D.Sc.**

LITTLE information appears to have been published about the diffusing power of unpolished surfaces. The subject has been studied by optical measurements by Zöllner and others, chiefly for astronomical purposes; and the radiation from such surfaces has also been investigated with apparatus designed for measuring radiant heat. But the influence of such diffusion in increasing the illumination of rooms and open spaces, although well known, does not appear to be appreciated to the extent that its importance deserves; and a few numerical determinations of the coefficients of reflexion, absorption, and transmission of diffusing surfaces may prove of interest.

Terms in light are used vaguely, and it will not be deemed out of place to define those which will be here needed. By the *reflecting power* of a surface is meant the ratio of the amount of light reflected by it to the total amount of light incident upon it. The *illumination* of a surface is the amount of incident light per unit area of the surface. The unit *quantity of light* is the flux of radiation per second across a unit area of a sphere of unit radius at whose centre a unit light (of one candle) is placed. The amount of light radiated by a source of k candle-power, within a solid angle Ω, is $k\Omega$, and the total quantity of light emitted by it is $4\pi k$. The *brightness* of a diffusing surface is its candle-power per unit

* Communicated by the Physical Society: read Dec. 9, 1892.

area in the direction normal to the surface. The illumination produced at a point by a surface of brightness B, subtending a (small) solid angle Ω at the point, is $B\Omega$, and if a surface, containing this point, have its normal inclined at an angle ϕ to the axis of Ω, the illumination of this second surface due to the first is $B\Omega \cos \phi$.

If B is the brightness of a surface rendered luminous by reflexion, if η is its (diffused) reflecting-power, and if I is the illumination of the surface, then

$$\pi B = \eta I. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This relation follows from the assumption of the law of cosines, viz. that the candle-power (per unit area) of a bright surface is $B \cos \phi$ in a direction making an angle ϕ with the normal. The right-hand member of (1) is by definition equal to the whole light reflected from unit area of the surface, and must be equal to the integral of $B \cos \phi \, d\Omega$ for all directions on one side of the surface. The value of the integral is easily seen to be πB.

The brightness of a body, as just defined, is directly proportional to the illumination of the image of the body on the retina of the eye, and the word may thus be quite justly used in the ordinary physiological sense of the term. Similarly the law of cosines, just alluded to, is merely another way of expressing the fact that the sensation of the brightness of a diffusing surface is the same from whatever direction this surface may be viewed. For the amount of light received by the eye, and concentrated on the image on the retina, is simply the product of the area of the pupil of the eye and the illumination at the surface of the eye due to the bright object. The former factor is constant for different directions of view, and the latter must vary as the solid angle subtended by the object at the eye, since the area of the image on the retina is a measure of this solid angle. The illumination at a point at which a surface of brightness B subtends a solid angle Ω is not necessarily $B\Omega$ for all inclinations of Ω to the surface, unless the law of cosines is fulfilled; and, if this law is fulfilled, it follows that the illumination of the image of this surface on the retina of the eye is constant at all distances and inclinations. The eye is a good judge, and is indeed the only judge, of quick variations in brightness, and the cosine law is always applicable to diffusing surfaces, the appearance of which does not alter as the eye moves past them. Any divergence from this law is negligible so far as its influence on illumination is concerned.

If Q is the quantity of light radiated per second by the

light-sources within a room, and if Q' is the total amount of light falling on the walls,

$$Q' = Q + \eta Q'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For of the quantity Q', a portion $\eta Q'$ must be reflected, and the rest absorbed, and the rate at which light is absorbed by the walls must be equal to the rate at which it is produced. The average illumination I' of the walls of the room must hence be related to I, the illumination due to the direct action of the lights, by the equation

$$I' = \frac{1}{1-\eta} I. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus if $\eta = \cdot 90$, $I' = 10\,I$, and if $\eta = \cdot 50$, $I' = 2\,I$, so that the illumination due to the walls of the room may become far more important than that caused by the direct rays of the lights.

The truth of this relation may be also seen as follows:—The light Q falling on the walls is partially reflected, and a quantity ηQ is sent back into the room. This light falls on the walls again and a portion $\eta \times \eta Q$ is reflected a second time. The total quantity of light Q' falling on the walls owing to successive reflexions is given by the equation* .

$$Q' = Q + \eta Q + \eta^2 Q + \ldots = \frac{1}{1-\eta} Q.$$

Or, again, as the illumination I_p' of the walls at any point P is made up of a portion I_p due to the direct rays of the lights, together with a part caused by radiation from the walls, we have

$$I_p' = I_p + \int B \cos\phi \, d\Omega, \quad . \quad . \quad . \quad . \quad (4)$$

where B is the brightness of the walls, and ϕ is the inclination of the solid angle $d\Omega$ to the normal to the surface at the point P. Assuming that the brightness is the same all over the bounding surface of the room, the value of the integral is readily seen to be πB, and this, as already shown, is equal to $\eta I'$, where I' is the average illumination of the walls.

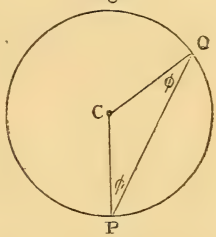
When the bounding surface of a room or enclosure consists of portions whose reflective powers are different, the average reflective power may be taken as

$$\eta_m = \frac{\eta_1 A_1 + \eta_2 A_2 + \&c. \ldots}{A}, \quad . \quad . \quad . \quad . \quad (5)$$

* Since writing this paper I have discovered that this relation has been already pointed out by Mascart [see Palaz, *Traité de Photométrie Industrielle*, p. 268].

where A is the total area of the bounding surface, of which a portion A_1 has a reflective power equal to η_1, and a second portion A_2 a reflective power η_2, &c. This relation is very approximately true for ordinary rooms, and may be shown to be quite accurate for a spherical enclosure.

Fig. 1.



For let P and Q be any two points of a sphere of centre C and radius r (fig. 1). Then $PQ = 2r \cos \phi$, where ϕ is the angle which the chord makes with the radius through either P or Q. Also, with the same notation as before, we have

$$I_p' = I_p + \int B \cos \phi \frac{dA \cos \phi}{PQ^2},$$

where dA is an element of area at Q of brightness B, and subtending a solid angle $dA \cos \phi / PQ^2$ at P. Now $PQ^2 = 4r^2 \cos^2 \phi$ and $\pi B = \eta I'$, where I' is the illumination of the area dA: hence

$$I_p' = I_p + \frac{1}{4\pi r^2} \int I' \eta dA = I_p + \frac{1}{A} \int I' \eta dA, \quad . \quad (6)$$

A being the total area of the spherical surface. The integral is constant whatever the position of the point P, and whatever the character of the reflecting surface of the sphere. Thus if any complete [or if any portion of a] spherical surface be illuminated in *any* manner I_p by the direct rays of a combination of light sources, the actual illumination I_p' will exceed I_p by a constant amount all over the sphere, owing to the reflective action of the surface. Also, if the original distribution be uniform all over the sphere, $I_p = I$, a constant, I_p' will also be constant, $= I'$, and

$$I' = I + \frac{I'}{A} \int \eta dA = I + \eta_m I',$$

where

$$\eta_m = \frac{\Sigma \eta dA}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

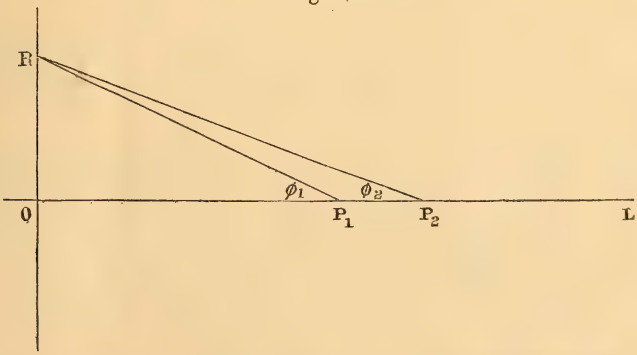
Taking as an average case for rooms a reflecting power of 70 per cent. for the ceiling, 40 per cent. for the walls, and 20 per cent. for the floor, the average value of η is a little over 40 per cent., and the increase of illumination by reflexion becomes as much as 70 per cent. If the walls and ceiling of a room be well whitewashed, the average reflecting power will not fall far short of 80 per cent.; and in such cases the illumination due to diffused reflexion is four times as important as that caused by the direct action of the lights in the room. A further great advantage, resulting from the use of good diffusing surfaces, arises from the fact that the illumination they cause is, in most cases, very approximately constant all over the room, and does not cast shadows.

It is to be noted that when a reflecting surface is coloured, its average reflecting power does not properly represent the character of the increase of illumination caused by it. A room whose walls are covered with red paper whose average reflecting power is 40 per cent., may quite possibly have the red light in the room increased five times owing to the action of the walls. Suppose, for instance, that the reflective power of the paper for red light is 80 per cent., and for other kinds of light only 10 per cent., the average reflecting power will not exceed 40 per cent., yet the red light will be increased five times, while other kinds of light will not be increased to any perceptible extent.

Measurements of Reflective Power.

The surface, whose reflective power was required, was attached to a large screen of black velvet placed at one end O of a 3-metre photometer-bench OL (see fig. 2), so as to

Fig. 2.



be perpendicular to its length. Two lights were used, one being a Methven two-candle gas standard, placed at L, and

the other a glow-lamp run generally at about 20 candle-power, placed at P_1. A Lummer-Brodhun photometer was slid along the bench to a point P_2 at which the illumination due to reflexion from the surface OR was equal to that due to the Methven standard at L. At first the lamp P_1 was permanently situated a little to one side of the bench, and the rays from it in the direction of the photometer P_2 were screened off. Subsequently the points P_1 and P_2 were made to coincide, the lamp being fixed to the same slider as the photometer and suitably screened from it and from the eyes of the observer. In some experiments the distance OL was kept fixed and the position of balance OP was determined for each surface tested. In other cases both OP and OL were varied.

Let:—

A = area of diffusing surface on screen OR (centre at O).
Ω_1, Ω_2 = solid angles subtended by A at P_1, P_2 respectively.
x_1, x_2 = distances OP_1, OP_2 respectively.
y = distance P_2L.
K = candle-power of the glow-lamp at P_1.
k = candle-power of Methven standard at L.

Then:—

The quantity of light falling on the area A is $K\Omega_1$,
the average illumination of A is $K\Omega_1/A$,
the average brightness is $\eta K\Omega_1/\pi A$, by (1),
the illumination at P_2 is $\eta K\Omega_1\Omega_2/\pi A$,
and also the illumination at P_2 is k/y^2;

whence

$$\eta = \frac{k}{K}\frac{\pi A}{\Omega_1\Omega_2 y^2} = \frac{k}{K}\frac{\pi x_1^2 x_2^2}{A y^2}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

provided the dimensions of A are small compared with x_1 or x_2. When this is not the case, the equation (8) is not sufficiently correct, and a more accurate formula may be obtained as follows, by taking note of the inclination of the rays to the surfaces.

The illumination of the surface at the point R due to the lamp at P_1 can be easily shown to be $K\cos^3\phi_1/x_1^2$, where ϕ_1 is the angle between RP_1 and OL, the line of centres of the bench. The brightness B of the surface at R is therefore $\eta K\cos^3\phi_1/\pi x_1^2$ by equation (1). An element of area dA at R subtends at P_2 a solid angle $d\Omega_2$ equal to $\cos^3\phi_2 dA/x_2^2$, and the illumination at P_2 due to this element is $B d\Omega_2 = \eta K\cos^3\phi_1\cos^3\phi_2 dA/\pi x_1^2 x_2^2$ on any area placed perpendicular to RP_2. As the photometer screen is perpendicular to the

bench and not to RP_2, we must multiply this expression by $\cos\phi_2$ to get the effective illumination due to the element dA. Finally we have for the total illumination the integral:—

$$I=\frac{\eta K}{\pi x_1^2 x_2^2}\int \cos^3\phi_1 \cos^4\phi_2\, dA, \quad . \quad . \quad . \quad . \quad (9)$$

in which the angles ϕ_1, ϕ_2 are related by the equation

$$x_1 \tan\phi_1 = x_2 \tan\phi_2.$$

When the area A is circular, with O as its centre, this integral reduces to

$$I=\frac{\eta K}{x_1^2}\int \cos^3\phi_1 d\,.\sin^2\phi_2. \quad . \quad . \quad . \quad (10)$$

The value of this integral can be readily evaluated, but it does not lead to a convenient formula, and as it was found practically preferable to fix the lamp to the same slider as the photometer, and at the same distance from the screen OR, we may put

$$\phi_1 = \phi_2 = \phi,$$

$$x_1 = x_2 = x,$$

and (10) then reduces to

$$I=\eta\frac{K}{x^2}\frac{2}{5}[1-\cos^5\phi], \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which ϕ is the semiangle of the cone with base A and height x.

This expression is rendered more convenient for purposes of calculation by taking advantage of the fact that $A/\pi x^2$, or $\tan^2\phi$, is a small quantity. By neglecting $\tan^6\phi$ compared with unity we obtain

$$\frac{2}{5}[1-\cos^5\phi]=\frac{1}{X},$$

where

$$X=\frac{\pi x^2}{A}+1{\cdot}75+{\cdot}43\frac{A}{\pi x^2}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and in most cases it will be found that the third term in this expression is negligibly small compared with the sum of the other two.

The value of I found in (11) may be equated to k/y^2 when the photometer is in the position of balance, and on doing so, we find for η the value

$$\eta=\frac{k}{K}\frac{x^2}{y^2}X, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which reduces to (8) when x is large.

This equation was used for the great majority of the reflexion tests. With feebly diffusing surfaces such as black cloth, the distance x had to be so much reduced that the area A subtended a greater angle at the photometer screen than the aperture of the photometer itself. In such cases the angle ϕ in (11) was calculated from the solid angle subtended by the aperture of the photometer at the centre of the photometer screen. With diffusing surfaces which appeared to shine slightly under the action of light the effect of regular reflexion had to be separated from that of diffused reflexion, by experiments made with the same surface for different values of x. In such cases, which will be alluded to subsequently, the true reflecting-power is not given by formula (13). The areas A of the reflecting surfaces used in the experiments were never circular, as assumed in the above proof, but as they were always approximately square, with the central portion at O (fig. 2), any error in (12) and (13) arising in this way must be quite negligible. The ratio k/K of the two lights was frequently tested in the course of the experiments and was found very constant during every set of tests.

The results obtained are given in the accompanying table. In the majority of cases the numbers given are approximate only, as there seemed no object in aiming at great accuracy. The first four surfaces referred to in the table, viz., thick white blotting-paper, white (rough) cartridge-paper, tracing-paper, and tracing-cloth, were, however, carefully tested, and the numbers obtained represent the mean of many observations.

TABLE I.—Reflecting-Powers.

	per cent.		per cent.
White blotting-paper	82	Plane deal (clean)	40 to 50
White cartridge-paper	80	,, (dirty)	20
Tracing-cloth	35	Yellow cardboard	30
Tracing-paper	22	Parchment (one thickness)	22
Ordinary foolscap	70	,, (two thicknesses)	35
Newspapers	50 to 70	Yellow painted wall (dirty)	20
Tissue-paper (one thickness)	40	,, ,, ,, (clean)	40
,, (two thicknesses)	55	Black cloth	1·2
Yellow wall-paper	40	Black velvet	0·4
Blue paper	25		
Dark brown paper	13		
Deep chocolate paper	4		

Zöllner found white surfaces to reflect from 70 to 78 per cent. of the light incident upon them. The numbers given at the head of the above table are slightly higher. They, however, agree very well with results which have been pub-

lished with regard to the diffuse reflexion of radiant heat, since 82 per cent. is generally given as the reflective power of white substances*.

The degree of consistency of the results may be judged as follows :—In a series of 10 determinations of the reflective power of white blotting-paper, made with values of x (see fig. 2), varying from 40 cm. to 82 cm., the mean reflecting power was found to be 82·4 per cent., and the average error of a single determination from the mean was 1·4. With surfaces of lower reflecting-power (such as tracing-cloth) the numbers obtained in successive experiments were more consistent. The value of η for white blotting-paper was checked by comparing it directly with that of a piece of common mirror. The Methven standard at L (see fig. 2) was replaced by the mirror, arranged so as to reflect the light from the glow-lamp along the line of the bench. The reflective power of the white blotting-paper placed on the screen OR was found to be 98·5 per cent. of that of the mirror. The value of η for the mirror, for normal rays, was separately determined and found to be 82 per cent., and hence η for the blotting-paper comes out as 80·8 per cent.

Several of the numbers in the above table were confirmed by comparative measurements, using white paper as a standard reflector, the Methven standard at L (fig. 2) being replaced by a surface of white paper exposed to the rays of the glow-lamp at P. The reflective power of one of the walls tested was measured in diffuse daylight by exposing the aperture of a photometer to the radiation of the wall, and balancing the illumination against that of a standard candle. The part of the wall affecting the photometer was then covered with a sheet of white blotting-paper, and the ratio of the two illuminations at once gave the ratio of the reflecting-powers.

Measurement of Absorption.

The absorbing-powers of some of the preceding substances were determined by measuring the candle-power of the light from a glow-lamp, first when this was uncovered, and afterwards when it was surrounded with a cylinder of the paper under test. The cylinders were short, being just longer than the height of the lamp, and were closed at top and bottom with caps of the same paper, so that the lamp was completely

* See Jamin et Bouty, Tome Troisième, p. 149. Results by MM. Goddard, De la Provostaye et Desains.

enveloped by the paper tested. The ratio of the diminution of candle-power to the original candle-power gave the *apparent* absorption of the paper. If the candle-power in some particular case was found to diminish 30 per cent., it would have been erroneous to conclude that the envelope absorbed as much as 30 per cent. of the light incident upon it, or that 70 per cent. was transmitted. If the reflecting, absorbing, and transmitting powers of a material be respectively denoted by η, a, and τ, there must exist between these quantities the relation

$$\eta + a + \tau = 1.$$

Also if Q be the quantity of light given out per second by the light-source within the envelope, the quantity of light incident per second upon the surface of the envelope will, owing to internal reflexion, be increased to Q′, where

$$Q'(1-\eta) = Q;$$

the quantities of light absorbed and transmitted will respectively be

$$aQ' \text{ and } \tau Q',$$

and the ratios these quantities bear to Q will similarly be

$$\frac{a}{1-\eta} \text{ and } \frac{\tau}{1-\eta};$$

the sum of course being unity.

If the light-source can be assumed to radiate equally in all directions, the ratio of its candle-power, after putting on the envelope, to the original candle-power will not be τ but $\tau/(1-\eta)$. The influence of internal reflexion is to increase *both* the absorption and the transmission, and unless it is taken into account large errors may be made in estimating the coefficients. A very simple way of showing the effect of internal reflexion consists in surrounding a glow-lamp with a white paper cylinder, open at the top, and adjusting a photometer screen till the illumination caused by it is balanced against that of some standard source of light. If now a piece of white paper be placed on the top of the cylinder, so as to shut in the vertical rays of the lamp, the candle-power in the horizontal direction will be found to increase considerably. In some of the tests, in order to avoid error caused by non-uniform radiation of the lamp, this was first surrounded with an envelope of tracing-cloth, or blotting-paper, and the combination used as the light-source. If k_0 be its candle-power in this condition, and if k_1 be the observed candle-power after completely surrounding it with an envelope of the sub-

stance to be tested, the apparent absorption of this material is

$$\frac{k_0 - k_1}{k_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and the true absorption coefficient α is given by

$$\alpha = (1 - \eta)\frac{k_0 - k_1}{k_0}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where η is the previously found reflexion coefficient.

When an inner envelope is used to produce a light which radiates equally well in all directions, it is necessary for the outer envelope to be large compared with it, since otherwise the formula for the increase of illumination due to internal reflexion cannot be applied.

The following table gives the values of the absorbing coefficients, expressed as percentages, for the four substances at the head of Table I., from which the corresponding values of η used in applying (15) have been taken.

TABLE II.

	Apparent Absorption.	Real Absorption.
White Blotting-paper	77 per cent.	13·8 per cent.
White Cartridge-paper	61 ,,	12·2 ,,
Tracing-cloth	23 ,,	15·0 ,,
Tracing-paper	9 ,,	7·0 ,,

Three large glass globes, made for arc-lamps, were also tested. As the reflective powers of the globes could not easily be found, only the apparent absorption was measured. One globe was of opal glass (almost transparent), and the ratio of apparent absorption was 15 per cent. A second globe was of ground glass and absorbed 42 per cent. The remaining one was of opal glass, too opaque to allow any bright object placed within it to be distinguished. This absorbed 39 per cent.

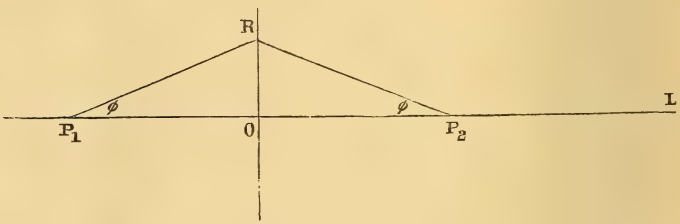
Measurements of Transmitting-Power.

The amount of light transmitted through the surfaces above mentioned was measured in a very similar manner to that in which their reflective powers were determined; the

only difference being that the glow-lamp at P_1 (see fig. 2) was moved to the opposite side of the surface as in fig. 3.

OR represents the screen of paper, pinned on a wooden frame, and placed perpendicular to the optical bench P_1L. The

Fig. 3.



$OP_1 = OP_2 = x \quad P_2L = y.$

glow-lamp was at P_1, the photometer at P_2, and the Methven standard at L. The distances OP_1, OP_2 were arranged to be equal, and balance obtained by moving L along the bench. On referring to equations (8) to (13) and the arguments used in establishing them, it will be seen that they are all applicable to the case now considered if only we substitute τ, the transmitting-power, for η.

When, however, tests were made with the paper surfaces already referred to, it was soon found that the numbers calculated from expression (13),

$$\frac{k}{K}\frac{x^2}{y^2}X = Y, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

were not constant for the same substance. They differed from each other far more than could be accounted for by errors of experiment; thus, the values found for τ by this formula were too high, and frequently exceeded 100 per cent. For any given surface the values were found to increase progressively with the value of x used in the tests. The reason for this is easily seen when it is remembered that equations (8) to (13) are only true on the assumption that the surfaces considered are purely diffusive, and do not alter in appearance as the eye changes its point of view. When light is transmitted through a semitransparent substance such as tracing-paper, or tracing-cloth, the brightest part of the surface is always on the line joining the eye to the light, and visibly moves over the surface as the point of view is changed. The

easiest way to represent these facts is to assume that, of the light transmitted, a portion τ_1 passes through without change of direction, and that the rest τ_2 is diffused in accordance with the cosine law. The case is analogous with a reflecting surface such as white enamelled iron, which reflects a portion η_1 of the incident light in accordance with the regular law of reflexion, and diffuses another portion η_2 according to the law of cosines. On referring to equations (8) to (11) it will be noticed that they are still true for the illumination due to diffusion if we substitute for η either τ_2 or η_2 (according as we are considering transmission (fig. 3) or reflexion (fig. 2) respectively). The additional illumination at the photometer due to regular, *i. e.* direct, transmission (transparency) is

$$\tau_1 \frac{K}{(2x)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and a similar expression holds for regular reflexion if we substitute η_1 for τ_1.

The whole illumination must, as before, be equal to k/y^2, and by (11), (12), and (17) we have

$$\tau_2 \frac{K}{x^2 X} + \tau_1 \frac{K}{4x^2} = \frac{k}{y^2}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

whence the value of Y in (16) is equal to

$$Y = \tau_2 + \frac{\tau_1}{4} X; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and a similar expression holds for reflexion if we replace τ_1 and τ_2 by η_1 and η_2 respectively. The true values for the transmitting and reflecting coefficients are

$$\left.\begin{aligned} \tau &= \tau_1 + \tau_2, \\ \eta &= \eta_1 + \eta_2, \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and the reason the values found for Y were too high, and became greater and greater as x increased, was simply that the values used for X (see 12) were always greater than 4, and increased rapidly with x.

By plotting the numbers found for Y with the corresponding values of X, a straight line is obtained from which the values represented by the symbols in (20) can all be determined. The straightness of these lines, and the verification of the fundamental formula

$$\eta + \alpha + \tau = 1,$$

affords a good criterion of the extent to which the principles and the formulæ, referred to in this paper, can be relied upon.

The following Tables III., IV., and V. contain the results of three sets of tests on the transmitting-power of blotting-paper and tracing-cloth, and on the reflecting-power of tracing-cloth. The values of $Y_{obs.}$ are calculated with the aid of (12) and (16) from the observed values of x and y. All the dimensions are given in centimetre-units. In the accompanying sheet of curves the values of $Y_{obs.}$ are plotted as ordinates, with the corresponding values of X as abscissæ. From the straight line most nearly representing the connexion between the points the values of $Y_{calc.}$ have been obtained, and are given in the tables. From this straight line also the true value of the transmitting (or reflective) power can be found by finding the value of the ordinate when X = 4. The intercept on the axis of Y shows the portion of the light which is diffused.

TABLE III.—Transmitting-Power of Blotting-paper.

A=980. K=26. k=2. τ=9·2. $Y_{calc.}$=6·50+2·7 X/4.

x	60	50	40	45	55	60
y	154	120	88·4	104·6	137	154
X	13·6	9·8	7·0	8·25	11·40	13·6
$Y_{obs.}$	15·5	13·2	11·2	12·0	14·4	15·5
$Y_{calc.}$	15·7	13·1	11·2	12·1	14·2	15·7

TABLE IV.—Transmitting-Power of Tracing-cloth.

A=980. K=23·1. k=2. τ=54·4. $Y_{calc.}$=41·0+13·4 X/4.

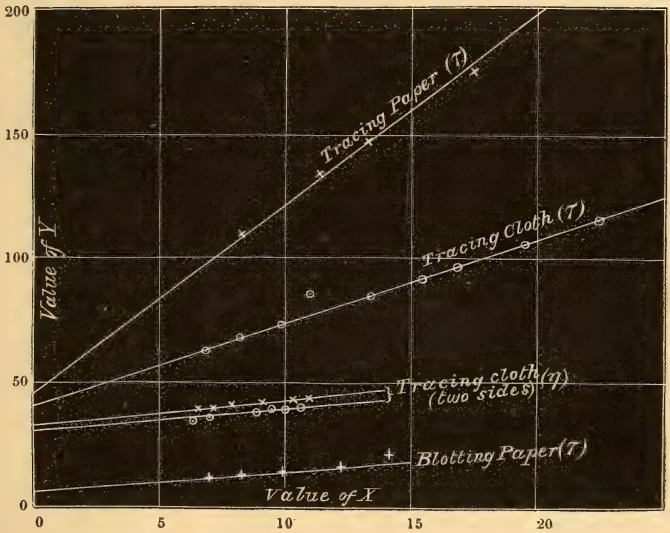
x	40	50	60	70	80	75	65	55	45
y	39·2	53·5	70·1	89·4	105·6	95·8	77·7	61	46·1
X	6·98	9·80	13·6	17·4	22·30	19·4	15·4	11·2	8·25
$Y_{obs.}$	63·5	74·3	86·1	97·0	116	107	91·8	81·7	69·3
$Y_{calc.}$	64·4	73·7	85·6	99·2	115·8	106	94·0	78·5	68·7

TABLE V.—Reflecting-Power of Tracing-cloth (shiny side).

$A=1300.\quad K=12.\quad k=2.\quad \eta=35{\cdot}7.\quad Y_{calc.}=30{\cdot}9+4{\cdot}8\,X/4.$

x	50	55	62·3	59·8	47·5	44·5
y	90	104·4	127·7	120·2	82·5	75·5
X	7·82	9·10	11·13	10·45	7·22	6·55
$Y_{obs.}$	40·4	41·8	44·1	43·2	39·6	38·6
$Y_{calc.}$	40·3	41·8	44·2	43·4	39·6	38·7

Fig. 4.



Several sets of tests were taken. Some of these are represented by the sheet of curves shown in fig. 4. Y is the percentage of the incident light which the surface *apparently* reflects or transmits, assuming that it is all diffused, and is calculated from equation (16). The true values of the coefficients are obtained from the curves by applying equations (19) and (20). The numerical details of the observations are of no special interest, and the essential results may be summarized as follows :—

TABLE VI.—Reflective Powers.

	Regular. η_1.	Diffused. η_2.	Total. η.
Blotting-paper	0 per cent.	82 per cent.	82 per cent.
Cartridge-paper	0 „	80 „	80 „
Tracing-cloth (shiny side) ...	4·8 „	30·9 „	35·7 „
„ „ (rough side)...	2·7 „	31·6 „	34·3 „
Tracing-paper	2·2 „	19·8 „	22·0 „

TABLE VII.—Transmissive Powers.

	Direct. τ_1.	Diffused. τ_2.	Total. τ.
Blotting-paper	2·7 per cent.	6·5 per cent.	9·2 per cent.
Cartridge-paper	2·5 „	8·7 „	11·2 „
Tracing-cloth	13·4 „	41·0 „	54·4 „
Tracing-paper	29·8 „	46·2 „	76·0 „

We may now collect the coefficients η, α, τ, determined by the foregoing independent methods, and compare their sum with unity.

TABLE VIII.

	η.	α.	τ.	$\eta+\alpha+\tau$.
Blotting-paper	82 per cent.	13·8 per cent.	9·2 per cent.	105·0 per cent.
Cartridge-paper ...	80 „	12·2 „	11·2 „	103·4 „
Tracing-cloth	35 „	15·0 „	54·4 „	104·4 „
Tracing-paper	22 „	7·0 „	76·0 „	105·0 „

The numbers in the last column differ from the true value of 100 per cent. to a greater extent than can fairly be accounted for by the limits of experimental error. They are all over 100; and this was the case, not only for the tests here given, but also for every one of many sets of tests taken. The small discrepancy would be accounted for by assuming that the law of cosines is not exactly fulfilled. A very slight departure from this law would be amply sufficient to explain the results.

Suppose the candle-power of a unit area of a diffusing surface in the direction of the normal is B, and in any

direction ϕ is $$B(\cos\phi)^{1+\epsilon}.$$

It is then easy to show that the total amount of light given out per unit area is equal to

$$\pi B \frac{1}{1+\frac{\epsilon}{2}}.$$

In all the above experiments the actual measurements have referred to the light receding from the diffusing substance at inclinations all practically normal to its surface. The quantity B has been measured, the total light has been calculated as πB, and has been overestimated in the ratio $1+\frac{\epsilon}{2}:1$.

To account for an error of 5 per cent., the quantity ϵ need only be 0·1. The brightness of the surface (in the physiological sense) would, when viewed at an inclination ϕ, be proportional to

$$B(\cos\phi)^{1+\epsilon}/\cos\phi, \quad \text{or} \quad B(\cos\phi)^{\epsilon}.$$

This quantity is practically constant (if $\epsilon=0{\cdot}1$) until ϕ becomes very large. Its value is ·994 for $\phi=20°$ and ·974 for $\phi=40°$, and the change in the brightness of the surface would hardly be perceptible to the eye.

This correction applies to the coefficients η_2 and τ_2; it does not affect the values of η_1, α, or τ_1. In some of the first tests of reflecting-power the inclination of the light-rays to the surface was considerably less than 90 degrees, and the values of η obtained were less than those given above. These tests confirm the idea that the cosine law is not strictly fulfilled, but they were not accurate enough to be conclusive.

The above measurements were all made in the Optical Laboratory of the Central Institution, and the writer has had the benefit of the assistance of some of the students of that College in re-testing and confirming the results given in the foregoing tables.

XIII. *Relation of Volta Electromotive Force to Pressure &c.* *By* Dr. G. Gore, *F.R.S.**

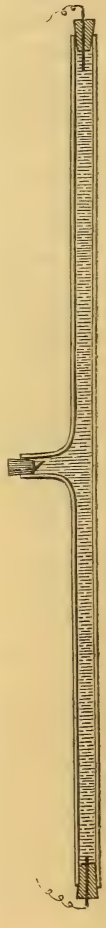
FORTY-TWO years ago I made several experimental attempts to discover a difference of molecular state of the upper and lower ends of a vertical column of solution of cupric sulphate:—1st. By suddenly reversing the ends of a gutta-percha tube, about 6 feet high and 6 inches diameter, filled with the liquid, by swinging the tube in a vertical

* Communicated by the Author.

Note. Compare Wild's experiment (Wiedemann's *Galvanismus*, 1872, vol. i. p. 776; Pogg. *Ann.* 1865, vol. cxxv. p. 119).

plane upon a transverse horizontal axis at its centre, the ends of the tube being formed of two similar plates of electrolytic copper connected with a galvanometer; and 2nd, by simultaneously raising and lowering two similar disks of copper in a tall column of such solution, the disks being attached to the galvanometer and suspended from the two ends of a cord passed over a pulley. These attempts, however, were not successful owing to disturbing influences at the surfaces of the plates, and to the employment of an insufficiently sensitive galvanometer. Recently I have renewed the experiments in a somewhat different form, and have succeeded in obtaining definite though small effects; only minute ones were anticipated.

Fig. 1.



The arrangement usually employed was as follows:—A single glass tube (or several), about 3 metres long and 1 centim. bore, securely fixed upon a board, was fitted with corks and two wire electrodes of the same kind of metal at its two ends, and filled within ·5 centim. with an electrolyte (see fig. 1). It was then placed horizontal, so that the bubble of air receded into the branch of the tube; the two electrodes were then connected with a Thomson's reflecting-galvanometer of 3040 ohms resistance, and the tube allowed to remain undisturbed until all sign of current or of variation of current ceased. It was then placed vertical, and as soon as a steady permanent deflexion occurred its direction and amount was noted; the tube was then placed either horizontal until all current ceased, or at once placed vertical with its ends reversed, and the amount of maximum steady deflexion again recorded.

In many cases five such tubes were fixed upon the board and connected in series, the upper electrode of one to the lower of the next one, in order to multiply the effect, and as many of them charged with an electrolyte and connected with the galvanometer as was desired.

The electrodes were fixed in the corks by means of melted shellac, and the corks were saturated with melted paraffin. By employing suitable metals and electrolytes, making each pair of electrodes of metal cut from immediately contiguous parts of the same piece, and including in each instance a wire coil of 50,000 ohms resistance in the circuit, the fluctuations

of the current were reduced to a minimum, and the needles usually settled at or near zero in about 5 or 10 minutes after closing the circuit with the tubes in a horizontal position. No perceptible amount of interference was caused by the small difference of temperature, usually equal to about 1°·5 C. of the upper and lower parts of the experiment room. All the experiments were repeated two or three times in order to ensure reliable results.

The solutions employed were all of them made with distilled water, and were in nearly all cases dilute; the exact strength used, however, was not a matter of much importance. Those of the halogens usually contained about 3·29 grains of chlorine, 7·41 grains of bromine, or 11·25 grains of iodine in 18 ounces of water. Those of the acids contained about 55 grains of absolute acid in 40 ounces of water; and those of neutral salts or of alkalies contained about 300 grains of the substance to that amount of water. The electrodes of cadmium, zinc, aluminium, tin, lead, and copper were formed of thick wire; and those of nickel, iron, silver, gold, and platinum were thin wires. The following Tables give the particulars and the results.

TABLE I.

Effect of Varying the Electrolyte only.
With Electrodes of Zn.

No. of Expt.	Substances.	Grains per oz.	No. of Tubes.	Amount of Deflexion.
1.	Cl	·164	5	8° ↑
2.	Br	·37	,,	0
3.	Cl+KCl	·18+8·3	2	50° ↑
4.	Br+KBr	·37+ ,,	,,	28° ,,
5.	I+KI	·62+ ,,	,,	12° ,,
6.	Cl+KCl	¼ sat. soln.+9·4	4	150° ,,
7.	Br+KBr	6 drops+ ,,	,,	Very variable.
8.	I+KI	3 grains+ ,,	,,	20° ↑
9.	HCl	·68	5	0°
10.	HBr	·92	,,	,,
11.	H_2SO_4	1·6	,,	,,
12.	HNO_3	1·2	,,	,,
13.	$HClO_3$	·75	,,	,,
14.	$HBrO_3$	?	,,	,,
15.	HIO_3	2·5	,,	,,
16.	Acetic Acid	2·1	,,	,,
17.	Tartaric ,, ...	3·7	,,	,,
18.	Oxalic ,, ...	,,	,,	,,
19.	$HClO_3+KClO_3$ ..	1·0+7·5	3	20° ↑
20.	HCl+AmCl	·65+7·5	5	0°

Table I. (*continued*).

No. of Expt.	Substances.	Grains per oz.	No. of Tubes.	Amount of Deflexion.
21.	KCl	7·5	5	15° ↑
22.	KBr	,,	,,	Small ↑
23.	KI	,,	,,	0°
24.	$KClO_3$	,,	,,	40° ↑
25.	$KBrO_3$	2·5	,,	0°
26.	KIO_3	7·5	,,	,,
27.	KNO_3	,,	,,	,,
28.	K_2SO_4	,,	,,	,,
29.	$KHSO_4$	,,	,,	20° ↑
30.	K_2CrO_4	,,	,,	0°
31.	$K_2Cr_2O_7$	,,	,,	,,
32.	$KMnO_4$	,,	,,	,,
33.	$KHCO_3$	,,	,,	,,
34.	K_2CO_3	,,	,,	,,
35.	KHO	,,	,,	15° ↑
36.	NaCl	7·5	5	0°
37.	NaBr	,,	,,	10° ↑
38.	NaI	,,	,,	0°
39.	$NaClO_3$	,,	,,	25° ↑
40.	$NaNO_3$	,,	,,	0°
41.	Na_2SO_4	,,	,,	15° ↑
42.	$NaHCO_3$	,,	,,	0°
43.	Na_2CO_3	,,	,,	0°
44.	NaHO	,,	,,	10° ↑
45.	AmCl	7·5	5	0°
46.	AmBr	,,	,,	12° ↑
47.	$AmNO_3$	,,	,,	40° ↓
48.	Am_2SO_4	..	,,	25° ↑
49.	AmSesquicarb.	,,	,,	0°
50.	AmHO	,,	,,	0°
51.	$BaCl_2$	7·5	5	10° ↑
52.	$BaBr_2$	,,	,,	10° ,,
53.	BaI_2	,,	,,	0°
54.	$Ba2BrO_3$	,,	,,	,,
55.	$Ba2NO_3$	,,	,,	20° ↑
56.	$SrCl_2$	7·5	5	15° ↑
57.	$Sr2NO_3$	,,	,,	40° ,,
58.	$CaCl_2$	7·5	5	20° ↑
59.	$MgCl_2$	7·5	5	16° ↑
60.	$MgSO_4$	,,	,,	0°
61.	$ZnCl_2$	7·5	5	0°
62.	$ZnBr_2$	,,	,,	,,
63.	$ZnSO_4$	,,	,,	,,
64.	Al_23SO_4	7·5	5	0°
65.	Distilled water	32 oz.	5	0°

Table II.

Effect of Varying the Electrodes and Liquids.
With Electrodes of various Metals.

No. of Expt.	Substances.	Grains per oz.	No. of Tubes.	Amount of Deflexion.
66.	Al with Cl+KCl.	¼ sat. soln. +9·4	4	20° ↑
67.	„ „ Br+KBr.	6 drops + „	„	30° „
68.	Cd with Cl+KCl.	¼ sat. soln. +9·4	4	20° ↑
69.	„ „ Br+KBr.	6 drops + „	„	20° „
70.	„ „ I+KI ...	3 grains + „	„	30° „
71.	Sn with Cl+KCl.	¼ sat. soln. +9·4	1	10° ↓
72.	„ „ Br+KBr.	6 drops + „	„	0°
73.	Pb with Cl+KCl.	¼ sat. soln. +9·4	1	0°
74.	„ „ $KClO_3$ ...	7·5 grains.	3	0°
75.	Fe with Cl+KCl.	¼ sat. soln. +9·4	1	20° ↑
76.	Co „ „ + „	„ + „	„	35° „
77.	Ni „ „ + „	„ + „	„	50° „
78.	Cu „ „ + „	„ + „	4	50° „
79.	„ „ Br+KBr.	6 drops + „	„	0°
80.	Ag „ Cl+KCl.	¼ sat. soln. + „	1	0°
81.	„ „ KCy	7·5	5	0°
82.	Au „ Cl+KCl.	⅛ sat soln. +9·4	1	30° ↑
83.	Pt „ „ + „	„ + „	„	„ ↑
84.	„ „ Br+KBr.	6 drops + „	„	0°
85.	„ „ HCl	1·6	4	„
86.	„ „ $KClO_3$ ...	7·5	2	„
87.	„ „ $KHSO_4$...	„	5	„
88.	„ „ KHO ...	„	„	„

Table III.

Equivalent Solutions.

No. of Expt.	Substances.	Grains per oz.	No. of Tubes.	Amount of Deflexion.
89.	Cd with Cl+KCl.	·18 gr. + 8·3 gr.	2	12°
90.	„ „ Br+KBr.	·37 „ + „ „	„	28°
91.	„ „ I+KI ...	·62 „ + „ „	„	10°

In experiments Nos. 17, 18, 20, 66, 67, and 70, evolution of gas and disturbances of the current occurred; and in Nos. 71, 72, and 73 the quantity of water employed was only 18 ounces.

In every case of production of current, provided the two electrodes were neutral whilst in the horizontal position, and were allowed to remain sufficiently long in each of the vertical ones, the two opposite currents produced were equal in amount. In all the cases in which a sudden change from the horizontal position (and a neutral state) to the vertical one was attended by production of a current, the maximum amount of deflexion of the needles usually occurred in about three minutes; but if in any case, whilst the tube was vertical, its ends were suddenly reversed, the reversal of the deflexion required a longer period of time to attain its maximum.

Degree of Permanence of the Currents.

With the object of ascertaining whether the currents were temporary or permanent, two of the tubes were fitted with zinc electrodes and a solution of $NaClO_3$ of the usual strength (see exp. 39) made with distilled water, which had been deprived of air by boiling. After having become neutral in the horizontal position, they were placed vertical and gave the following results:—

TABLE IV.

Influence of Time.

Number of experiment.	Minutes.	Deflexions.	Minutes.	Deflexions.	Minutes.	Deflexions.
92.	1st.	10° ↑	10th.	30° ↑	75th.	30° ↑
	2nd.	20 „	15th.	„ „	90th.	„ „
	3rd.	25 „	30th.	„ „	105th.	„ „
	4th.	30 „	45th.	25 „	120th.	„ „
	5th.	„ „	60th.	„ „	16 hours.	20 „

By subsequently placing the tubes horizontal to become neutral, and then erecting them again, the deflexion was 25° ↑. The results show that the action was of a comparatively permanent character, and that the currents were not due to dissolved air.

Influence of Strength of Solution.

In this case zinc electrodes and two solutions of the same substance of different degrees of concentration were employed.

The upper and lower ends of the tubes were wrapped in cotton-wool. The following are the particulars of the experiments :—

Number of experiment.	Substance.	Grains per oz.	Number of Tubes.	Amount of Deflexion.
93.	KCl	4·0	2	8 ↑
94.	„	40·0	„	12 „

These results show that the amount of deflexion was increased fifty per cent. by employing a solution of ten times the degree of concentration (compare also experiments Nos. 3 and 5 with 6 and 8). The cotton-wool had no apparent effect upon the amount of deflexion, thus showing that the unequal temperature of the upper and lower parts of the room had no perceptible effect.

Period of Time required for Reversal.

With zinc electrodes in the solution of $KClO_3$ (exp. 24) and three tubes, the period required to attain the maximum effect after a complete reversal was 4·5 minutes, and was the same after standing vertical 15 hours.

With zinc electrodes in the solution of Na_2SO_4 (exp. 41) and three tubes the time required to completely reverse was 10 minutes, and in the solution of KCl (exp. 21) it was 15 minutes.

With cadmium in the same solution of KCl it was 13 minutes, and after standing vertical 18 hours it was again 13 minutes.

The degree of fixity of the state produced varied, therefore, both with different liquids and with different metals, but not with lapse of time.

Degree of Electromotive Force of the Current.

This was measured by the method of balance with two thermoelectric couples of iron and German-silver wires, the junctions of which were immersed in melted paraffin at 120° C., the outer ends of the wires being at 20° C. With zinc electrodes in two tubes and the solution of four grains of KCl per ounce of water, giving a deflexion of 8 degrees, as in exp. 93, the electromotive force was equal to ·00572 volt. Wild (see note, *ante*) attempted to find the variation of

electromotive force of amalgamated zinc in a solution of zinc sulphate by increase of pressure of about two thirds of an atmosphere, and observed that it was in any case less than one 400,000th of that of one Daniell's cell, = about ·0000028 volt (compare exp. 63). He apparently failed to discover the phenomenon of the current by not happening to select a suitable electrolyte.

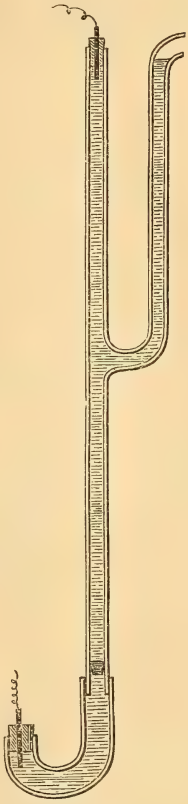
General Results.

On examining Tables I., II., III., and IV. various facts may be observed :—1st. Currents were produced by using a large variety of metals as electrodes, and by employing various kinds of electrolytes. 2nd. The results varied both with the kind of liquid and with that of metal. 3rd. In every one of the cases in which the liquid employed was a diluted acid alone no current was observed, and the addition of a salt to the acid appeared to have no effect unless the salt alone gave a current (compare exps. 19, 20, 24, 45). 4th. Out of 91 experiments 41 gave perceptible currents ; probably in many other cases currents were produced, but were too feeble to be detected. 5th. Out of the 41 cases in which a current occurred, in 39 it was in an upward direction and in 2 downward. 6th. The current continued many hours without sensible diminution. 7th. In every case the current was extremely small, and required a few minutes to attain its maximum amount. 8th. It was much smaller with a dilute solution than with a concentrated one. 9th. The largest current occurred with zinc in a solution of Cl and KCl, probably in consequence of the great chemical energy of the combination and the small amount of resistance. 10th. By adding to a solution of Cl some KCl, or to one of Br some KBr, a larger current was obtained than with either liquid singly, probably in consequence of diminution of resistance. 11th. Solutions of iodides frequently gave smaller currents than those of bromides, and bromides less than chlorides ; there are, however, numerous exceptions to this statement. And 12th. Vibration of the lower electrode by means of a tuning-fork had no apparent effect upon the maximum current.

Influence of Equal Pressure at the two Electrodes.

In order to ascertain whether the current was produced during the absence of any difference of pressure at the two electrodes, I employed one of the usual tubes, 3 metres high, having a porous biscuit-ware diaphragm $\frac{5}{16}$ inch thick near

Fig. 2.



its lower end, offering such a degree of hindrance as to almost entirely prevent the flow of the liquid, whilst allowing the electric current to pass, and provided with a bent glass tube at its lower end to receive the lower electrode (see fig. 2). In order to prevent any diminution of pressure at the upper electrode an open branch-tube was provided, as shown; and to obviate any increase of pressure at the lower one, a minute nick in the side of the lower cork allowed any of the liquid which had passed through to overflow: only one drop of the liquid, however, was forced through by the pressure in about one hour. Sufficient hindrance to the passage of the liquid was obtained by coating the whole of each end of the diaphragm with varnish, except a minute portion of the surface about 1 millim. diameter. A perfectly clean diaphragm was employed in each case, and it was soaked in the liquid previous to use. Only a single tube with zinc electrodes was employed in each experiment.

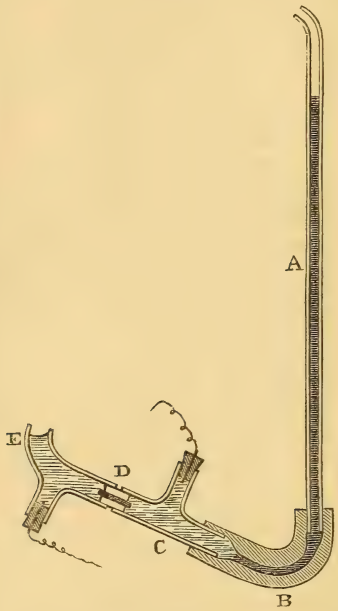
Two experiments were made, one with a solution of 18·7 grains of chlorate of potassium and the other with 18·7 grains of nitrate of strontium per ounce of preboiled water, and although the circuit was complete no current was produced by placing the tube vertical in either case (compare exps. 24 and 57). These results prove that the current was not produced during the absence of difference of pressure.

Influence of Difference of Pressure without Difference of Altitude.

In order to test whether difference of pressure alone was sufficient to produce a current, the following arrangement was employed (see fig. 3). A, pressure-tube containing mercury; B, very thick tube of indiarubber; C, glass tube with a branch containing a zinc-wire electrode securely fixed in it by means of a cork and shellac; D, porous-ware diaphragm $\frac{5}{8}$ inch long and $\frac{1}{8}$ inch diameter fixed in a cork; E, a second branch-tube containing the other similar electrode. The diaphragm was sufficiently impervious to allow not more than one drop of the

electrolyte to pass per hour whilst under the pressure of a vertical column of 30 inches of mercury. The electrolyte

Fig. 3.



was a solution of 18·7 grains of chlorate of sodium per ounce of water, and was allowed to completely saturate a perfectly clean diaphragm previous to the experiment being made. The entire arrangement was fixed upon a board.

After placing the tube A horizontal until the two electrodes became neutral it was quickly raised to the vertical position: a current and deflexion of 10 degrees was gradually produced in about three minutes. This current was permanent, but gradually diminished to 6 degrees on removing the pressure. Several trials were made, and in each case the electrode which was under pressure was positive to the other. By repeating the experiments with a pressure of 52 inches height of mercury, a deflexion of 12 degrees was obtained. The experiments were repeated with the apparatus modified by having a glass tube about 3 metres long fixed to the end E and filled with the electrolyte, with the second electrode transferred to its distant end: whether this glass tube was horizontal or vertical, the effects of varying the mercurial pressure were substantially the same as in the previous experiments. These results show that difference of pressure alone was sufficient to

produce the currents. In all these experiments, and in the previous ones in which a diaphragm was employed (see fig. 2), the latter manifestly diminished the amount of the current.

Influence of Thermoelectric Action.

It might be supposed that the stronger pressure at the lower electrode, by giving rise to greater chemical heat, is attended by a thermoelectric current from that electrode to the electrolyte; and this view is apparently supported by the circumstances:—1st, where the chemical energy is greatest the current is usually the strongest; 2nd, the full strength of the current is developed gradually; and, 3rd, the current is a continuous one. But it does not agree with the fact, established by numerous and varied experiments, that whilst heat usually makes metals more electropositive in solutions of alkaline salts and alkalies, it makes them more negative in those of acid salts and acids (see "The Thermoelectric Properties of Liquids," Proc. Roy. Soc. 1878, vol. xxvii. p. 513). If heat therefore was the cause, downward currents would have occurred in the latter group of liquids, instead of which no currents occurred in dilute acids, and upward ones were produced in solutions of acid salts.

In order to finally settle this point, I made the following experiments:—Two vertical metal wires, 2 inches long, coated with shellac over about an inch of their length at about half an inch from their ends, were immersed three-fourths of an inch in two portions of the electrolyte contained in two small glass beakers placed about 3 inches asunder, the two portions of liquid being connected together by a piece of clean linen tape previously soaked in the solution and laid upon a strip of sheet-glass connecting the edges of the two vessels; each beaker contained a thermometer, and the wires were connected with the usual galvanometer. After the needles of the galvanometer had settled at zero, heat was applied to one of the beakers until the temperature of the liquid had risen about 3 or 4 Centigrade degrees, and the effect was then noted.

With zinc and the solution of $KHSO_4$ of exp. 29, no perceptible current occurred, but in that of $NaClO_3$ of exp. 39 a deflexion of 20° was produced, the warm metal being negative. With platinum in the $KHSO_4$ solution, and in that of KHO, no current was perceptible (compare exps. 87, 88). These results together with those previously mentioned clearly prove that the currents obtained were not due to thermoelectric action.

General Remarks and Conclusions.

The currents were manifestly occasioned by difference of pressure at the upper and lower electrodes, and apparently by that circumstance alone. They were not due to the unequal temperatures of the room or to heat evolved by the pressure at the lower electrode, nor to air or impurities dissolved in the water, nor to bubbles of gas &c. adhering to the electrodes, nor to greater conduction resistance of the electrolyte in a downward than in an upward direction, nor to difference of altitude of the electrodes except so far as it affected the difference of pressure; nor were the deflexions caused by mechanical disturbances of the galvanometer or by any magnetic substance near it. They were also not produced by thermoelectric action due to greater chemical heat at the lower electrode. In all the cases in which a diaphragm was employed, the electric current due to pressure was not perceptibly affected by any current produced by flow of the electrolyte through the partition; the considerable conduction resistance of the septum, however, largely reduced the quantity of the current due to pressure.

The results of the experiments in general indicate that the upper and lower ends of a column of an electrolyte are not in exactly the same physical or chemical state; that a fixed difference of condition of the liquid and metal was gradually produced when the tube was placed vertical, and that this condition required several minutes in order to attain its maximum. That both the metal and the liquid are altered by the pressure is shown, not only by the fact that a change of either affects the amount (and in some cases also the direction) of the current, but also by the circumstance that the period of time required to reverse the condition, and the current, by reversing the tube varies with a change of metal as well as of liquid. These circumstances are interesting, and indicate the gradual production by pressure of a state of mechanical stress of the lower electrode and of the liquid near it; and as action and reaction are always equal and opposite, the state of stress of the metal must be attended by one of counter stress of the liquid. The same states of stress might of course be produced by means of a hydraulic press, a lever, &c., or by centrifugal action during rapid whirling of the tube. As the increase of pressure and stress at the lower electrode was followed by the production of a permanent electric current, it must also have been followed by increased energy of chemical union of the metal and liquid

and an increase of electromotive force at that electrode; the three kinds of pressure—mechanical, chemical, and electrical—varying directly together. The greater mechanical pressure at the lower electrode enabled the liquid and metal to chemically unite with greater energy, and thus permitted that electrode to become electropositive to the other. The fact that the strongest currents were usually obtained by the use of the most energetic chemical substances further support the view that the phenomenon is partly chemical, and it is well known that certain substances will only chemically combine whilst kept under pressure together.

In all the cases in which the more positive metals, such as zinc, were employed, both the electrodes were visibly corroded; as, however, the electric current was excessively minute, only an extremely small proportion of this chemical action was inseparably associated with it; and as the currents were not due to ordinary chemical heat, any examination of the comparative losses of weight of the two electrodes by corrosion would probably have been of but little value.

The phenomena suggest some abstruse questions,—What is the most hidden cause of the current? Only a very fundamental cause could have produced so large a proportion as 95 per cent. of currents in one uniform direction. The original cause must lie in some change of the potential motion of the molecules; some kind of molecular energy must have been lost in order to produce the currents. The immediate cause was probably a small proportion of the potential energy of the motion of the superficial molecules which must have been transformed into current during chemical union of the metal and liquid, the other and far greater portion being directly changed into chemical heat. The questions why one portion is directly converted into electric current and another into heat, and why so largely into heat, I have not examined (compare Proc. Roy. Soc. 1884, vol. xxxvi. p. 331; also M. B. Raoult, *Ann. de Chim. et de Phys.* 1867, pp. 137–193).

We know that work is done during the act of putting on the pressure, and that this work may increase the energy of molecular motion; in addition to the energy communicated to the arrangement in this way, constant pressure may produce constant current if there is a continual yielding of the molecules to it; but as only motion can produce motion, and as unchanging pressure is a purely statical phenomenon, if there is no such yielding unvarying pressure cannot be a real cause of continuous current. We know also that the properties of substances and the molecular motions to which those

properties are due vary with every change of mechanical pressure. If, therefore, pressure alters the direction or the velocity of molecular motion, it may act as a permitting condition so as to enable some of the unceasing motion of the molecules to expend itself in producing a permanent current, like such motion does in a voltaic cell; and this appears to be a reasonable explanation. Contraction of total volume by chemical union, being a yielding to pressure, may contribute to the result in the present case.

As the production of current was conditional upon *difference* of pressure at the two electrodes, it must have been as much dependent upon the pressure and the state of molecular motion at one electrode as upon that at the other. And as we know that volta electromotive force is very intimately connected with velocity of the molecules, and that the two appear to vary directly together (see "A General Relation of Electromotive Force to Equivalent Volume and Molecular Velocity," Proc. Birm. Phil. Soc. 1892, vol. viii. pp. 63–138; The Electrical Review, vol. xxx. pp. 693, 722, 755, 786; and Phil. Mag. Sept. 1892, p. 307), it is probable that the greater degree of pressure at the lower electrode permits some of the molecules of liquid and metal to strike each other with greater velocity than at the upper one. It is worthy of notice that pressure has the same effect as dilution of the electrolyte, &c. upon volta electromotive force (*ibid.*); as dilution and pressure each separately increases volta electromotive force, and as dilution is apparently attended by an increase of velocity of the molecules, it is reasonable to conclude that pressure is probably attended by a similar effect. It would be interesting to investigate the relations of the current to the compressibility and elasticity of metals and electrolytes. The present results indicate that electromotive force may be due to unequal molecular pressure.

Whatever may be the manner in which the molecular motions are affected by pressure, whether by altering their direction or their velocity, the experiments of this research show that they are influenced in essentially the same way in 39 out of 41 instances, and it is evident that only some very fundamental cause could produce such a uniform effect. The fact that nearly all the currents are in one direction suggests that the real cause of electromotive force itself can only be about one stage more fundamental than the cause of the currents. In all cases the currents obtained were results, not only of a difference of electromotive force between the lower metal and liquid and the upper ones, but primarily of the

influence of pressure upon the electric potential of the metal alone and upon that of the liquid alone at each electrode.

It is probable that an investigation of the effect of pressure upon the electric potential of the metal alone and upon that of the electrolyte alone would yield more uniform results than that of its effect upon the electromotive force of the two substances in mutual contact, because the conditions would then be more simple ; but as the effect upon the potential produced by a single compression would be extremely small, a series of compressions, with the effects of them accumulated by means of an electric condenser as in an influence machine, would be necessary in order to render the effect manifest. Such a research would probably show that pressure increases the positive potential of positive substances and the negative potential of negative ones. As pressure increases electromotive force it must increase the two kinds of electric potential which constitute that force ; thus in a case where a current occurs with a closed circuit, the two potentials are always produced if the circuit is open. The facts also that the largest currents in the present research usually occurred with the most positive metals and the most negative electrolytes (see exps. 3 and 6), and the smallest frequently, though not invariably, happened with the most positive electrolytes (see exps. 33, 34, 42, 43, 49, 50), support this hypothesis. Some of the cases in which no appreciable current was produced, or in which reverse ones occurred, might have been due to the pressure increasing the electropositive potential of the liquid as fast as, or faster than, that of the metal.

Although some effect of the atomic or molecular weights of the substances employed upon the direction or magnitude of the currents must have occurred, none was observed (see Table III.) ; many additional experiments would probably be necessary to properly examine this question. I have not been able to suggest any explanation of the circumstance that diluted acids did not in any case produce a current ; nor have I been able to investigate in what manner the pressure may have affected the direction of motion of the molecules of the combining substances, but possibly some information might be obtained by examining the influence of pressure upon the thermal spectra of the substances and comparing the results with those obtained in this research. As the properties and molecular motions of substances vary with every change of temperature, it is probable that the electromotive force produced by unequal mechanical pressure would vary with the temperature of the metal and electrolyte.

Effect of Pressure upon Voltaic Couples.

In all the foregoing experiments the investigation was limited to the influence of pressure upon the electromotive force generated by a single kind of metal and a single kind of liquid, and did not include its influence upon that of ordinary voltaic couples composed of pairs of metals or pairs of liquids; it is evident, however, that the latter are only compound cases of the former. Gibault has already experimentally examined the effect of a pressure of 100 atmospheres on several kinds of voltaic cells, and obtained the following amounts of electromotive force in volts:—Daniell's cell (20 per cent. $ZnSO_4$) $+\cdot0005$; (27·56 per cent. $ZnSO_4$) $+\cdot0002$; Warren De la Rue cells (1·0 per cent. $ZnCl_2$) $+\cdot0007$; (40·0 per cent. $ZnCl_2$) $-\cdot0005$; Volta's cells $-\cdot06$; Bunsen's $-\cdot04$; Gas battery $+0\cdot8$ (*Comptes Rendus*, 1891, vol. cxiii. p. 465; The Electrician, 1891, vol. xxvii. p. 711). Owing to the greater complexity of the conditions in these experiments, the proportion of cases giving reverse effects was 30 per cent., or six times larger than in those with single metals in the present research.

In all such experiments with voltaic cells, we have to consider not only the effect of pressure at the positive metal, but also that at the negative one. The results obtained in the present research show that the direction of the current which occurs with zinc and other positive metals is the same as that with gold and platinum; so that the effect of pressure upon the negative metal of a voltaic couple would probably be in nearly all cases to produce a greater or less amount of counter electromotive force, which would either diminish or reverse the effect due to the positive one. The amount or balance of effect, therefore, obtained with a voltaic couple would usually be very much less than that with a single kind of metal; this conclusion is confirmed by the results of Gibault's experiments, in which the amounts of electromotive force obtained by a pressure of 100 atmospheres were very much less than those usually obtained in my experiments by a difference of pressure of only about 2 or 3 atmospheres. As the pressure alone attending the height of the liquid of a voltaic cell affects the electromotive force, it necessarily follows that the energy of such a cell is affected by gravity and varies with the altitude and geographical position of the cell.

XIV. *On Radiant Energy.* *By* B. Galitzine*.

§ 1. *Introduction.*

STARTING with the far-reaching ideas of Faraday, Maxwell † has developed his theory of dielectrics, in which, by the identification of light with electrical vibrations, he comes to the conclusion that a ray of light must exert a certain pressure in the direction of its propagation, this pressure being numerically equal to the energy contained in each unit of its volume. One half of this energy is present in the electric, and the other half in electromagnetic, form.

By an entirely different line of argument, derived from an application of the second law of thermodynamics, Bartoli ‡ has arrived at the same result. His paper is extremely interesting, and the method by which he proves the *existence* of the pressure of light is free from objections, at any rate in the form given to it by Boltzmann § in a more recent paper. But the process by which he calculates the numerical value of this pressure P appears to me to be wrong. Bartoli imagines a perfectly reflecting empty sphere of radius R, with a perfectly non-reflecting (black) sphere of very small radius r at its centre. Let Q be the quantity of energy which falls on each unit of surface of the outer sphere in unit time. Then if the radius of this sphere be decreased by δR, according to Bartoli the inner sphere receives an amount of heat $q = 2Q/V \,.\, 4\pi R^2 \,.\, \delta R$, where V is the velocity of propagation of light. In this expression $2Q/V$ is the energy contained in unit of volume. Whether the energy can be expressed so simply or not, is not evident without further explanation. For the case of a cylinder, $\frac{2}{V}$ times the energy which is received by any normal section of the cylinder does *not* represent the energy contained in unit volume, as we shall see later. Boltzmann ‖ has already pointed out that Bartoli does not appear to have considered the effect of rays with oblique incidence.

Bartoli goes on to say that, since the inner sphere has increased its energy by an amount q, the work done

* Translated from Wiedemann's *Annalen,* vol. xlvii. pp. 479–495 (November 1892), by James L. Howard, D.Sc.

† 'Electricity and Magnetism,' vol. i. p. 144; vol. ii. p. 393 (2nd edit.).

‡ *Sopra i movimenti prodotti dalla luce e dal calore e sopra il radiometro di Crookes* (Florence. Le Monnier, 1876). Also *Nuov. Cim.* [3] xv. pp. 193–202 (1884); Exner's *Repertorium,* xxi. pp. 198–207 (1885).

§ Wied. *Ann.* xxii. p. 33 (1884).

‖ *Tom. cit.* p. 35.

against the pressure of light, viz. $P \cdot 4\pi R^2 \cdot \delta R$, must be equal to this, and hence

$$P = \frac{2Q}{V}.$$

This conclusion appears to me to be wrong, although the result obtained by a different method of reasoning differs from Bartoli's formula only by a constant factor. Our system consists of the inner black sphere and the space between the two spheres, which also possesses a portion of the energy*. On reducing the outer sphere work is done; not because the energy of the absolutely black body is thereby increased—for all the energy gained by the inner sphere is taken from the space between the spheres—but because the whole energy of the system passes from a lower to a higher temperature.

Boltzmann† has also attacked the same question. Let E be the heat radiated from unit surface in unit time (Boltzmann denotes it by $\phi(t)$); then he finds for the pressure P of light against a perfectly reflecting wall the expression

$$P = \frac{\pi}{V}\left[T\int\frac{\frac{dE}{dT}}{T}\,dT - E\right],$$

or

$$P = \frac{\pi}{V}\left[T\int\frac{\frac{dE}{dT}}{T^2}\,dT\right],$$

T being the absolute temperature. He writes the constant of integration equal to zero. This formula enables us to calculate the pressure P numerically for any assumed law of radiation. The method by which Boltzmann obtains his formula is quite a legitimate one, but I differ from him as to the value of the numerical factor. The subject may be treated in a more simple manner, as I shall proceed to show.

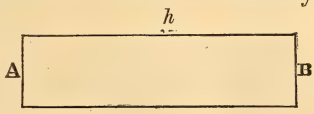
In conclusion I may draw attention to a paper by Lebedew‡, who has made a very interesting application of the Maxwell-Bartoli theory, by comparing the force of repulsion due to radiation with universal gravitation§.

§ 2. *Deduction of the Formula for the Pressure of Light* P.

Imagine an empty cylinder A B, of length h, whose walls

* *Cf.* Thomson, Phil. Mag. [4] ix. p. 36 (1855).
† Wied. *Ann.* xlv. p. 292 (1892). ‡ *Tom. cit.*
§ *Cf.* also Koláček, Wied. *Ann* xxxix. p. 254 (1890).

and base B, are perfect reflectors, and in which B can be displaced after the manner of a piston. A is an absolutely black body which may be replaced, when necessary, by a perfectly reflecting wall.



For simplicity, let the area of the cross section of the cylinder be unity.

Let us denote by ϵ the emissivity of our black body, *i. e.* the quantity of heat which unit surface of it radiates out in a normal direction every second. In a direction making an angle ϕ with the normal to the surface the emissivity will be smaller, namely $\epsilon \cos \phi$. To obtain the total quantity of heat E radiated from a unit of surface each second we require to evaluate the following integral*:—

$$E = 2\pi\epsilon \int_0^{\pi/2} \cos \phi \sin \phi \, d\phi = \pi\epsilon, \quad . \quad . \quad . \quad (1)$$

in which both ϵ and E are functions of the absolute temperature T only†.

Now let us calculate the quantity of energy e in unit volume of our cylinder when the black surface A is at temperature T. First of all imagine the cylinder to extend to infinity on the right, and let e' denote the energy contained in unit volume in this case.

We have obviously

$$e = 2e'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the surface sent out all its energy E in a normal direction, we should have

$$e' = \frac{E}{V},$$

or

$$e = \frac{2E}{V}.$$

But in reality a quantity of heat $2\pi\epsilon \sin \phi \cos \phi \, d\phi$ is radiated at an angle lying between ϕ and $\phi + d\phi$. The velocity V_ϕ with which this energy is propagated in a direction parallel to the axis of the cylinder is, according to the laws of reflexion, equal to $V \cos \phi$. The amount of energy in unit volume will thus be greater, and we shall have, as soon as equilibrium is established,

$$e' = 2\pi\epsilon \int_0^{\pi/2} \frac{\sin \phi \cos \phi}{V_\phi} \, d\phi = 2\pi\epsilon \frac{1}{V} = \frac{2E}{V};$$

* *Cf.* Wüllner, *Lehrbuch der Experimental-Physik*, iii. p. 238 (4th edition, 1885).

† *Cf.* Kirchhoff, Pogg. *Ann.* cix. p. 275 (1860).

or, from (2),

$$e=\frac{4E}{V}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

e is likewise a function of T only (Kirchhoff). E denotes the amount of energy which crosses any section of the cylinder in a given direction during unit of time. In order, therefore, to obtain the amount of energy contained in unit of volume, we must multiply the quantity E, not by 2/V, but by 4/V. (*Cf.* Introduction.)

If P is the pressure exerted on the base B, we have

$$P=T\int_0^T \frac{1}{T}\frac{de}{dT}dT-e.$$

First Proof.

Let the piston B be in contact with A, and keep A at temperature T. Now let the piston B be moved as slowly as possible through a distance h. The amount of heat Q imparted to the system, assuming the masses of A &c. to be infinitely small, is given by

$$Q=eh+Ph.$$

All quantities of heat are expressed in mechanical units.

If, now, we gradually reduce the temperature of A to zero, all the energy will be transferred from the cylinder to other bodies. When this has been done, let B be pushed back again to A without expenditure of work. The process is reversible, and as A's mass is infinitely small the second law of thermodynamics gives us the following equation:—

$$\frac{Q}{T}=\int_0^T \frac{dQ}{T},$$

$$\frac{e+P}{T}h=\int_0^T \frac{h\frac{de}{dT}}{T}dT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or

$$P=T\int_0^T \frac{\frac{de}{dT}}{T}dT-e, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which was to be proved.

This formula differs, however, from that of Boltzmann by a constant factor. For, substituting for e its value from (3),

$$P=\frac{4}{V}\left[T\int_0^T \frac{1}{T}\frac{dE}{dT}dT-E\right]; \quad . \quad . \quad . \quad (6)$$

whereas, according to Boltzmann,

$$P=\frac{\pi}{V}\left[T\int_0^T\frac{1}{T}\frac{dE}{dT}dT-E\right]. \quad . \quad . \quad . \quad (6a)$$

Second Proof.

Start with B at a distance h from A, and let A have temperature T. Let us take T and h as independent variables.

Consider, now, how much heat dQ must be given to the system when T increases by an amount dT, and h by dh. The work done in this case is Pdh, and

$$dQ=d(he)+Pdh\,;$$

or

$$dQ=(e+P)dh+h\frac{de}{dT}dT.$$

The increase of entropy dS is therefore

$$dS=\frac{dQ}{T}=\frac{e+P}{T}dh+\frac{h}{T}\frac{de}{dT}dT.$$

It follows from this, since according to the second law dS must be a perfect differential, and since e is a function of T only, that

$$\frac{dP}{dT}-\frac{P}{T}=\frac{e}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation is an immediate consequence of equation (4), from which it may be obtained by differentiation.

On integrating equation (7) we obtain

$$P=T\left[C+\int_0^T\frac{e}{T^2}dT\right],$$

or

$$P=T\left[C_1+\int_0^T\frac{1}{T}\frac{de}{dT}dT\right]-e. \quad . \quad . \quad . \quad (8)$$

To make this formula agree with (5) we must put the constant C_1 equal to zero, which appears perfectly legitimate. We shall indeed see later that P is proportional to e. If, then, for infinitely small values of T, e is proportional to any power of T, say $e=AT^n$, the assumption $C_1=0$ is clearly equivalent to the condition $n>1$.

Third Proof.—This proof rests upon the consideration of a complicated cyclical process, which is the same in principle as that of Boltzmann. I have merely introduced a slight alteration, and drawn further conclusions from the equation which expresses the first law of thermodynamics.

Suppose the piston B to be at A. Move B through a distance h_1, the temperature of A being always kept at T_1.

Let the heat required be Q_1. Then, as in the first case,

$$Q_1 = e_1 h_1 + P_1 h_1.$$

e_1 and P_1 denote respectively the energy contained in unit volume, and the light or heat pressure, at temperature T_1.

Now let A be replaced by a perfectly reflecting wall, and let the piston B be moved further away to a distance h_2. In this process an amount of work τ will be done, but as the operation is an adiabatic one the temperature must gradually decrease from T_1 to T_2.

$$\tau = \int_{h_1}^{h_2} P\, dh. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The principle of conservation of energy gives us

$$e_1 h_1 - e_2 h_2 = \int_{h_1}^{h_2} P\, dh; \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or, for an infinitely small displacement,

$$-d(eh) = P\, dh. \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

This having been done, we can again replace the reflecting wall A by a perfectly black surface, and either (1) gradually reduce this surface to zero temperature, and then, without doing any work, push the piston B back to A; or (2) keep the black surface at constant temperature T_2 and then bring back the piston B to A against the constant pressure P_2 (this latter being Boltzmann's operation). The last process necessary to complete the cycle is the heating of A to temperature T_1; this requires no energy, as its mass is infinitely small. In both cases the cycle of operations is reversible. Applying formula (4), the second law of thermodynamics gives us the following set of equations:—

$$\frac{e_1 + P_1}{T_1} h_1 = h_1 \int_0^{T_1} \frac{1}{T} \frac{de}{dT} dT = \frac{e_2 + P_2}{T_2} h_2 = h_2 \int_0^{T_2} \frac{1}{T} \frac{de}{dT} dT. \quad (11)$$

From these we obtain

$$\frac{e_2 + P_2}{T_2} h_2 - \frac{e_1 + P_1}{T_1} h_1 = 0,$$

or

$$d\left(\frac{e + P}{T} h\right) = 0,$$

$$d(eh) + P dh + h dP - \frac{h}{T}(e + P) dT = 0;$$

or, having regard to (10a),

$$\frac{dP}{dT} - \frac{P}{T} = \frac{e}{T},$$

thus leading us back to equation (7) again.

Equation (10*a*) enables us to find a relation between T and h for adiabatic processes. As e, and therefore P, are functions of T alone, it follows from (10*a*) that

$$h\frac{dT}{dh} = -\frac{e+P}{\frac{de}{dT}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or from (7),

$$h\frac{dT}{dh} = -T\,\frac{\frac{dP}{dT}}{\frac{de}{dT}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We can also obtain these formulæ by a comparison of the two integrals in equation (11). These give

$$d\left\{h\int_0^T \frac{1}{T}\frac{de}{dT}\,dT\right\} = 0,$$

$$dh\int_0^T \frac{1}{T}\frac{de}{dT}\,dT + h\,\frac{1}{T}\,\frac{de}{dT}\,dT = 0,$$

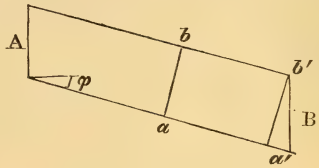
or

$$h\frac{dT}{dh} = -\frac{e+P}{\frac{de}{dT}}.$$

In order to evaluate the expressions in equations (5) and (13), we should require to know the relation between radiating power and absolute temperature. But if a direct relation between P and e could be found by any means, it would enable us to obtain directly the unknown law of radiation by integrating equation (7). As I have said before, I do not consider Bartoli's argument to be tenable. I have not succeeded in discovering a relation between P and e from purely mechanical considerations. Maxwell also, according to his own confession, was equally unsuccessful*. But the relation sought for may be deduced from the principles of the electromagnetic theory of light, and indeed by a simple application of Maxwell's fundamental conceptions to our case, as Boltzmann† was the first to show. I should like to give a slightly different proof of Boltzmann's relation, however.

* Maxwell, 'Electricity and Magnetism,' vol. i. p. 154 (2nd edit.).
† Wied. *Ann.* xxii. p. 291 (1884).

We know that a ray of light exerts a certain pressure along its line of propagation, which is numerically equal to the quantity of energy contained in unit of volume of the ray. If the beam is completely reflected the pressure is twice as great.



Suppose for greater generality s is the area of the radiating surface A, and consider those rays which are emitted with inclination ϕ to its normal. According to the laws of reflexion these will meet the other base B of our *straight* cylinder at the same angle, as is diagrammatically represented in the figure. The quantity of energy radiated at the angle ϕ is

$$dE = 2\pi\epsilon \sin\phi \cos\phi \, d\phi \, s.$$

We can assume all these rays to have the same direction. They exert on $a\,b$ or $a'\,b'$, which are perpendicular to their direction of propagation, a certain pressure dp', this being equal to dE/abV.

As $ab = s\cos\phi$, we have

$$dp' = \frac{2\pi\epsilon}{V} \sin\phi \, d\phi.$$

To every element of $a'b'$ there is a corresponding element of B, which is greater in the ratio of $\cos\phi$ to 1, and therefore the force acting on each unit of surface of B is $\cos\phi$ times smaller than dp'. Besides this, the force acts in a direction making an angle ϕ with the normal to B. It follows that the pressure exerted on B is

$$dp = dp' \cos^2\phi.$$

If B is a perfect reflector we must double the above expression in order to obtain the total pressure, and integrate for all values of ϕ between 0 and $\frac{\pi}{2}$. Hence

$$P = 2 \, . \, \frac{2\pi e}{V} \int_0^{\pi/2} \cos^2\phi \sin\phi \, d\phi,$$

or, from (3),

$$P = \tfrac{1}{3} e. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Formula (14) expresses the required relation.

We see, then, that P is proportional to e. If we substitute for P in formula (7), and then for e in equations (1) and (3), we find

$$\frac{d\epsilon}{dT} = \frac{4\epsilon}{T},$$

or

$$\epsilon = AT^4. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This is exactly Stefan's* law of radiation, which is thus deduced directly from the principles of thermodynamics and the electromagnetic theory of light, as Boltzmann has already indicated.

We have also

$$P = CT^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

a formula of which further use will be made in the following sections.

Equation (14) makes it possible for us to establish a more simple relation between h and T. From (13)

$$h\frac{dT}{dh} = -\frac{T}{3},$$

or

$$T = C_1 \frac{1}{\sqrt[3]{h}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

C_1 is determined by the initial conditions of the experiment.

It will be observed, then, that in adiabatic and reversible processes, such as we have just considered, the temperature varies inversely as the cube root of the volume.

§ 3. *The Meaning of Absolute Temperature.*

The energy contained in unit volume of our radiation-cylinder depends directly on the sum of all the electrical vibrations emitted at temperature T from the perfectly black surface, these being specified not by their wave-length, which is variable according to the nature of the external medium, but by their period or the number of vibrations per second, n. If $T=0$ we must have also $n=0$. But if T begins to increase new swings are constantly being added, and to every temperature there corresponds a certain maximum rate of vibration n_{max}, which the black body is capable of emitting at that temperature. Plainly n_{max} is a function of T.

$$n_m = \omega(T). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Let us suppose we are dealing with only one ray (the whole energy in unit volume will be obtained by integration

* Wien. *Ber.* lxxix. p. 423 (1879).

with respect to ϕ). If we start with the general equations of the electromagnetic field the electric force F_n at a point, which corresponds to any given time of swing, must be a periodic function of the time. Let the corresponding amplitude be a_n. If the force were constant we should have for the energy contained in unit volume

$$w = \frac{1}{8\pi} k F^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

k being the dielectric constant of the external medium.

But in our case F is variable. To every F_n there corresponds a particular dielectric constant k_n, but the energy in unit volume for these particular swings is clearly proportional to a_n^2. Since k may be put equal to unity for all swings *in vacuo*, the total energy per unit volume (e) is obtained as a sum of the following form,

$$e = \text{const.} \Sigma a_n^2,$$

the summation being extended to all vibrations which the body is capable of emitting at the temperature T.

a_n^2 is a function of T and n.

$$a_n^2 = f(\mathrm{T}, n). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The function f depends directly on the distribution of energy in the normal spectrum, the term "spectrum" including all possible rates of vibration.

If the energy is distributed in a continuous manner throughout the spectrum, the above summation becomes an integral.

Let $\phi(n)dn$ denote the probability of occurrence of waves whose rate of vibration lies between n and $n+dn$, then

$$e = \text{const.} \int_0^{n_m = \omega(\mathrm{T})} f(n, \mathrm{T}) \phi(n) dn. \quad . \quad . \quad . \quad . \quad (21)$$

For a perfectly black body which exercises no selective absorption, $\phi(n)$ is constant, but we may leave equation (21) in its more general form. From (15), (1), and (3) it follows that

$$\mathrm{T}^4 = \text{const.} \int_0^{\omega(\mathrm{T})} f(n, \mathrm{T}) \phi(n) dn. \quad . \quad . \quad . \quad . \quad (22)$$

The expression under the integral sign is a quantity which is proportional to the square of the corresponding electrical displacement.

We thus obtain the following result. The absolute tem-

perature depends directly on the sum total of all electrical displacements, and the fourth power of the absolute temperature is directly proportional to the sum of the squares of all the electrical displacements, these latter being calculated for vacuum.

The equation (22) enables us to solve another problem. If we differentiate it with respect to T_1, we have

$$T^3 = \text{const.}\left[\int_0^{n_m=\omega(T)} \frac{\partial f(n,T)}{\partial T}\,\phi(n)dn + f(n_m,T)\;\phi(n_m)\frac{d\omega}{dT}\right].$$

If the function f is known, that is if we know completely the distribution of energy in the spectrum, we are led to an equation of the form

$$\frac{\partial\omega}{\partial T} = F(\omega, T),$$

from which the unknown function ω can be determined.

The converse problem unfortunately cannot be solved; that is to say, a knowledge of the function ω tells us nothing concerning the distribution of energy in the spectrum, because $\partial f(n, T)/\partial T$ cannot be equated to zero*.

§ 4. *Relation between the Radiating Power and the Surrounding Medium.*

Let us now imagine our radiation-cylinder to contain some

* *Cf.* on this subject the following references:—Draper, Phil. Mag. [3] xxx. p. 345 (1847): Knoblauch, Pogg. *Ann.* lxx. pp. 205, 337 (1847): Jaques, Inaugural Dissertation Johns Hopkins University (Baltimore, J. Wilson & Son, 1879); *Beibl.* iii. p. 865 (1879): Stefan, Wien. *Ber.* lxxix. p. 423 (1879): Crova, *Ann. de Chim. et de Phys.* [5] xix. pp. 472-550 (1880): Langley, *Comptes Rendus*, xcii. p. 701 (1881); xciii. p. 140 (1881), and later papers: Desains, *Comptes Rendus*, xciv. p. 1144 (1882); xcv. p. 433 (1882); xcvii. pp. 689, 732 (1883): Lecher, Wied. *Ann.* xvii. p. 477 (1882): Christansen, Wied. *Ann.* xix. p. 267 (1883): Schleiermacher, Wied. *Ann.* xxvi. p. 287 (1885): Bottomley, *Beibl.* x. p. 569 (1886): H. Weber, Wied. *Ann.* xxxii. p. 253 (1887); *Math.-naturw. Mitth. aus den Sitzungsber. d. Berl. Akad.* xxxix. pp. 933, 565 (1888); *Beibl.* xiv. p. 897 (1890): Kövesligethy, Wied. *Ann.* xxxii. p. 699 (1887); *Astr. Nachr.* Nr. 2805, p. 329 (1887); *Abh. der ungar. Akad. der Wiss.* xii. Nr. 11; *Math. u. naturw. Ber. aus Ungarn*, iv. p. 9 (1887); v. p. 20 (1887); vii. p. 24 (1889); *Beibl.* xii. p. 346 (1888); xiv. p. 116 (1890): W. Michelson, *Journ. d. russ. phys.-chem. Ges.* [4] xix. p. 79 (1887); [6] xxi. p. 87 (1889); *Journ. de Phys.* [2] vi. p. 467 (1887); *Beibl.* xiv. p. 277 (1890): Emden, Wied. *Ann.* xxxvi. p. 214 (1889): Graetz, Wied. *Ann.* xxxvi. p. 857 (1889): Lord Rayleigh, Phil. Mag. xxvii. p. 460 (1889): Ferrel, *Sill. Journ.* [3] xxxix. p. 137 (1890); *Beibl.* xiv. p. 981 (1890): Edler, Wied. *Ann.* xl. p. 531 (1890): Violle, *Comptes Rendus*, cxiv. p. 734 (1892); *Journ. de Phys.* [3] i. p. 298 (1892).

diathermanous body whose dielectric constant for swings of frequency n is k_n. As the temperature remains the same, the range of frequencies is the same as before, namely, from $n=0$ to $n_m=\omega(\mathrm{T})$.

Equation (19) shows that the energy transferred across any section of the cylinder will be k_n times greater than before, for swings of frequency n, because the external medium takes part in the vibratory movement. Also, since the velocity of propagation V_n of these particular waves is smaller than in vacuum, the energy present in each unit of volume will be increased $k_n\mathrm{V}/\mathrm{V}_n$-fold; and if e_k is the total energy per unit volume we have, as in § 3,

$$e_k=\text{const.}\int_0^{n_m=\omega(\mathrm{T})} k_n\frac{\mathrm{V}}{\mathrm{V}_n}f(n,\mathrm{T})\phi(n)\,dn, \quad . \quad . \quad . \quad (23)$$

the constant having the same value as in equation (21), which may be looked upon as a special case of the more general equation (23).

If we neglect the effect of dispersion of the different waves we can write down the mean values k and V_k instead of k_n and V_n, and we thus obtain

$$e_k=k\frac{\mathrm{V}}{\mathrm{V}_k}e\ ;$$

or, having regard to equations (1) and (3),

$$\frac{4\pi\epsilon_k}{\mathrm{V}_k}=k\frac{\mathrm{V}}{\mathrm{V}}e=k\,\frac{4\pi\epsilon}{\mathrm{V}_k},$$

from which

$$\epsilon_k=k\epsilon.$$

This is exactly Clausius's law of radiation*, since, according to the electromagnetic theory of light, provided we neglect dispersion, we are perfectly justified in taking the square of the mean index of refraction as equal to the dielectric constant.

Clausius's law of radiation appears, then, to be a necessary consequence of Maxwell's fundamental conceptions.

§ 5. *Meaning of the Second Law of Thermodynamics.*

The above investigation of the radiant energy in a cylinder enables us to understand more clearly the meaning of the second law. In the course of the third proof of the formula

* Clausius, 'Mechanical Theory of Heat,' p. 314, § 10 (Macmillan, 1879); Bartoli, *N. Cim.* [3] vi. pp. 265–276 (1880); *Beibl.* iv. p. 889 (1880).

for the pressure of light we arrived at equation (10*a*). In that case the operation considered was an adiabatic one, and consisted in giving to a new portion of space, or let us say a new volume of æther dh, a quantity of energy

$$dq = e\,dh.$$

This transfer of energy to a new mass of æther is accompanied, as we have seen, by a certain expenditure of work Pdh. We have, then, two correlative phenomena, and in the limit, for infinitely small displacement, only $\frac{1}{3}$ of the energy transferred can be converted into external work. We have, indeed, from (14),

$$\frac{d\tau}{dq} = \tfrac{1}{3}.$$

The previous investigations enable us to calculate the same ratio for adiabatic displacements of finite magnitude; and this ratio is only a function of the initial and final temperatures.

From the same equation (10*a*) it follows that, if we wish to concentrate a certain quantity of energy into a smaller mass of æther, this can only be done by the expenditure of external work, the first law being obeyed throughout the process. In this lies the closer explanation of the second law.

From equations (10) and (9) we find, for finite displacements,

$$e_1h_1 - e_2h_2 = \tau = U_1 - U_2. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

U_1 and U_2 denote the quantities of energy in the cylinder at the beginning and end of the operation.

From equations (14), (16), and (17) it follows that

$$eh = 3CC_1{}^3T. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Insert this in equation (24) and note that $3CC_1{}^3$ may be determined from the initial conditions; we have

$$\tau = \frac{U_1}{T_1}(T_1 - T_2).$$

The available work is directly proportional to the fall in temperature (Second Law). It is only in the case of $T_2 = 0$, *i.e.* when the given quantity of energy U_1 is distributed over an infinitely great mass of æther (since according to (17) $T = 0$ only when $h = \infty$), that the whole energy can be transformed into external work.

In conclusion, let us compare the quantities of energy

present at the beginning and end of a *reversible* adiabatic operation. These give

$$\frac{U_1}{U_2} = \frac{e_1 h_1}{e_2 h_2}.$$

Substituting from (25) and (17),

$$\frac{U_1}{U_2} = \frac{\frac{1}{\sqrt[3]{h_1}}}{\frac{1}{\sqrt[3]{h_2}}}.$$

As h represents the volume (v) of the æther over which the given quantity of energy is distributed, the above equation may be written

$$U \sqrt[3]{v} = \text{constant}.$$

This is a statement which is probably capable of further extension. It expresses the fact that in adiabatic and reversible processes the quantity of disposible energy is inversely proportional to the cube root of the volume throughout which the energy is distributed. The statement does not involve the absolute temperature, but it really expresses the same principle as the second law of thermodynamics.

§ 6. *Summary of Results.*

1. Bartoli's proof is not admissible in all its details.

2. The application of the second law of thermodynamics enables us to calculate the pressure of light, as well as the changes of temperature in adiabatic and reversible operations (Boltzmann).

3. The fourth power of the absolute temperature is directly proportional to the sum of squares of all the electric displacements.

4. Clausius' law of radiation is an immediate consequence of Maxwell's fundamental conceptions.

5. The transfer of energy to new masses of æther is accompanied by the expenditure of work in the case of reversible operations.

6. In the case of adiabatic and reversible processes the amount of disposible energy is inversely proportional to the cube root of the volume throughout which this energy is distributed.

XV. *Some Experiments on the Diffusion of Substances in Solution.* By Spencer Umfreville Pickering, *M.A., F.R.S.**

THE following determinations of the comparative rates of diffusion of various non-electrolytes were intended to be preliminary to a more extended investigation, but, as I do not see my way at present to continue the work, I think it well to put on record those results which have so far been obtained.

Osmotic pressure is held to be due simply to the gaseous impact of the dissolved substance, and is therefore proportional to the number of molcules per unit volume, the temperature being constant. Now, by Graham's law, the rate of diffusion of a gas should be, *cæteris paribus*, inversely as the square root of its density, or of its molecular weight. Hence, at a given temperature and pressure the product of the molecular weight, m, by the square of the rate of diffusion, v, should be a constant. The relative values for v in the case of different bodies might be determined by simple diffusion-experiments if these could be conducted under perfect conditions: namely, the diffusing liquid remaining of a constant strength throughout, and the water into which diffusion is taking place remaining uncontaminated with the substance. The present results seem to show, either that the above supposition as to osmotic pressure is incorrect, or that the conditions obtainable in diffusion-experiments are very far from obtaining to ideal perfection; for the values deduced for mv^2 are by no means constant, even in those cases where the substances behave normally as to their osmotic pressure, *i.e.* where the solutions of equal molecular strength give the same osmotic pressure, this latter being measured by the depression exercised by them on the freezing-point of the water in which they are dissolved.

The method adopted was that termed by Graham jar-diffusion. The solutions under examination were placed in an open jar inside a large vessel of water, and the amount of substance which had diffused out of the former in a given time was ascertained by determining the strength of the remaining solution. The inner jars were beakers of a cylindrical form with ground flanges: they were ground also on the bottom, and rested on inverted ground-glass saucers placed in the centre of the large outer glass jars. Before being filled, each jar was placed in position and adjusted so

* Communicated by the Author.

that the mouth of the inner jar should be exactly level. The jars were marked so that they could be replaced in the proper position after being filled. When filled they were closed by glass plates with rods attached to them, and then lowered inside the larger jars which had previously been filled with water. The glass plates were then removed very slowly and carefully. At the end of the time allowed for diffusion the plates were replaced on the jars, the latter were removed from the water and the strength of their contents determined. Both the large and small jars were filled two days before the latter were placed inside the former, in order that the temperature of the cellar in which the determinations were made might be attained; and after the inner jars had been placed in position a further period of five hours was allowed before the glass plates were removed, so that any disturbance of temperature which had occurred in placing them in position might subside.

The capacity of the inner jars was 480 cubic centim., their internal diameter was 70 millim., and their internal height 125 millim. About three dozen of them were made, and of these the twelve which were found to be most uniform in size were used in the determinations. The extreme difference in the capacity of the largest and smallest of these twelve was 3·3 per cent., and the extreme difference of their superficies at the mouth was 3·8 per cent. The outer jars contained 12,000 cubic centim. of water, or twenty-five times the volume of the inner jars. The mouths of the jars were about midway between the surface and bottom of the water in the inner jars.

The strength of the solutions remaining in the jars at the end of the experiments was determined by means of their freezing-points. The solutions taken to start with were made up by weighing. The freezing-points of these, and also of weaker solutions obtained from them by dilution, were determined, and from these results the strength of any solution having a given freezing-point could be calculated. In order to minimize any errors due to possible irregularities of the freezing-points when plotted against composition, the solutions of known strengths, of which the freezing-points were determined, were selected so as to approach as nearly as possible to the strength of the solution left in the diffusion-jar.

The strength of the solutions taken was, as a rule, about 0·3 molecule to every 100 molecules of water, showing a depression of the freezing-point of water amounting to about 0°·3 ; about one third of the dissolved substance had diffused out by the end of the determination, the decrease in the

freezing-point measured being thus about 0°·1. The water into which the diffusion had taken place would at the end of the experiment contain only about 4 molecules of the substance to every 100,000 H_2O. These proportions had necessarily to be modified in several instances, and in such cases it was assumed that, in accordance with Graham's results (in support of which some of the present results may also be adduced), the rate of diffusion varied directly as the number of molecules present in a given volume of solution, or, more roughly, in a given weight of water.

The determinations were made in two separate series, marked (1) and (2) respectively in Table I., which contains the results. In the first series the temperature varied from 12°·1 to 15°·3, the time allowed being *probably* 18 days, the record of the exact time having been unfortunately lost: in the second series the temperature was 16°·0 to 18°·2, and the time was 25 days. Various steps were taken to estimate the magnitude of the probable errors. In the first place, the error due to any disturbance occurring in removing and replacing the glass plate from the inner jar was found to be inappreciable. A blank experiment in which these operations were performed showed that the solution of cane-sugar which the inner jar contained gave exactly the same freezing-point before and after the operations, *i. e.* within the estimation-figure of the thermometric reading, which was 0·05 millim. or 0°·0005. Secondly, in the first series duplicate determinations were made with each of the substances cane-sugar, acetic acid, and urea: the differences in the freezing-points of the solutions obtained in each pair were ·0011°, ·0062°, and ·0026° respectively, mean 0·0033°, or about 3 per cent. of the actual decrease measured, a quantity fully accounted for by the difference in size of the jars. Three per cent. in the actual decrease, however, represents only 1·24 per cent. in the proportional decrease (or actual decrease ÷ mean freezing-point), which is the quantity which is taken to represent the rate of diffusion v; and an error of 1·24 per cent. here will represent an error of 2·4 per cent. on the values of the supposed constant mv^2. Thirdly, glycerine solutions of the same strength were used in both series, and so also were cane-sugar solutions of nearly the same strength: the relative values for mv^2 in the two series were 1 : 2·586 in the case of glycerine, and 1 : 2·567 in the case of cane-sugar, the difference between the two ratios amounting to only 0·3 per cent.

The results of the diffusion-experiments are given in

Table I., the supplementary freezing-points necessary for the calculation of the strengths of the final solutions being given in Table II. (In the case of cane-sugar and acetic acid the determinations used for this purpose have already been published, *Berichte d. deutsch. chem. Gesell.* xxiv. p. 3329.)

The values in the table refer to the weight of anhydrous substance, the water of crystallization, whenever present, having been allowed for. This water, in the case of alloxan, was found to be $3H_2O$; whereas in the cases of gallic acid, tannin, and raffinose, 1, 2, and $5H_2O$ were taken as being respectively present. The proportional decrease of freezing-point or strength of the solution is the fraction which the actual decrease is of the mean freezing-point or strength. The molecular weight m' is deduced from the freezing-points in accordance with van't Hoff's formula

$$m' = \frac{\text{mean strength} \times 18{\cdot}9}{\text{mean f.-p.}}.$$

The values, it will be seen, agree fairly well in most cases with the theoretical molecular weights.

The sugars as well as the tannin and dextrin were obtained from Messrs. Trommsdorf. The dextrin, however, was doubtless very far from being pure (indeed pure dextrin has never yet been obtained), and very little weight can be attached to the results obtained with it. The sample of amylodextrin I owe to the courtesy of Mr. Horace Brown: unfortunately, however, the solution used deposited some of the substance during the experiments in the insoluble form, and hence the results with it are very doubtful; for not only is the mean strength of the solution uncertain, but the amount which had diffused out is also uncertain; for this had to be estimated in the diffusate, a large quantity of it being evaporated to a small bulk so as to obtain a depression of freezing-point sufficient for measurement; while, to correct for solids dissolved from the dish by the liquid during its evaporation, a similar volume of water was evaporated in the same manner. The calculated molecular weight of the amylodextrin was obtained from the freezing-point of the initial solution, and of that entered in Table II. The values which these gave were 2519·4 and 2452·8 respectively. The results with gallic acid are equally uncertain for a similar reason, the solution taken having been too strong, and having deposited crystals during the course of the experiment.

In the case of pyrogallol the liquid used to make the solu-

tion, and also that into which it diffused, was a very weak solution of sulphuric acid of which the freezing-point was 0°·0441. This prevented all but a trace of oxidation of the pyrogallol. The tannin used was probably not pure; but the difference in the calculated molecular weights deduced from the determinations in the two series is due to the solutions used being of different strengths, and to the fact that the molecular depression of the freezing-point diminishes rapidly as the strength of the solution increases. The depressions, I may mention, appear to show some marked irregularity; for when the four determinations (the two in Table I. at the initial strength, and the first two in Table II.) are plotted out, they do not all lie on any simple curve, either the determination at 12 parts to 100 giving much too small a value, or that at 16 parts too large a value. Another specimen of tannin was examined as to the freezing-points, and the results, which are the last four given in Table II., show the same peculiarity. This sample, however, gave throughout smaller values than that used in the diffusion-experiments, and the three stronger solutions of it deposited some tannin as well as ice in the freezing-point determination. The first sample did not do so.

In order to make the results of the first series more easily comparable with those of the second, the values for mv^2 obtained in the former have been multiplied by $2{\cdot}577(=x)$, in accordance with the results obtained with glycerine and cane-sugar, as mentioned above. The values for mv^2 are, as will be seen, very far from being constant. They vary from 16·09 with pyrogallol (omitting the doubtful result with gallic acid) to 46·81 with the weakest solution of cane-sugar; a variation of some 200 per cent., which cannot be in any way explained by the purely experimental error, since this, as has been mentioned, does not exceed 2 to 3 per cent. When we take the molecular weight deduced from the osmotic pressure (freezing-point) itself, m', instead of the theoretical molecular weight, the constancy is in most cases scarcely improved; and, indeed, in those three cases where these calculated molecular weights do not agree with the simple theoretical weight, the values for $m'v^2$ are made much less nearly constant, and attain the enormous proportions of from 72 to 260. This tends to show that there is a want of agreement between the values calculated for mv^2 from the depression of the freezing-point and the rate of diffusion.

Table I.—Results of the Determinations.

Substance.	Freezing-points of the Solutions.					Strength of Solutions.—Parts to 100 of Water by Weight.					Molecular Weight.		mv^2.	$m'v^2$.	Mol. Dep.
	Initial.	Final.	Mean.	Decrease.	Proportional decrease.	Initial.	Final.	Mean.	Decrease.	Proportional decrease.	Theoretical $=m$.	Calculated from f.-p. $=m'$.			
Acetic acid (1)	−·3692°	−·2675°	−·3183°	·1017°	·3195	1·142	·811	·977	·331	·3388	59·86	58·01	6·72 x=17·30	6·66=17·16	1·086°
Urea (1)	−·3410	−·2358	−·2884	·1052	·3648	1·068	·738	·903	·330	·3654	59·95	59·18	8·38 =21·60	7·90=20·36	1·066
Glycerine (1)	−·4434	−·3360	−·3900	·1068	·2739	2·140	1·621	1·881	·519	·2759	91·79	91·16	6·99 =18·01	6·94=17·88	1·060
„ (2)	−·4413	−·2845	−·3629	·1568	·4321	2·140	1·363	1·752	·777	·4435	„	91·25	18·06	17·95	1·059
Phenol (1)	−·3260	−·2483	−·2871	·0777	·2706	1·687	1·254	1·471	·433	·2944	93·78	96·84	8·13 x=20·95	8·39=21·63	1·019
Pyrogallol (2)	−·3394	−·2351	−·2873	·1043	·3630	2·428	1·691	2·060	·737	·3573	125·70	135·52	16·09	17·35	1·229
Alloxan (1)	−·2814	−·2174	−·2474	·0640	·2587	2·050	1·550	1·800	·500	·2778	141·74	136·41	10·94 x=28·19	10·53=27·13	1·085
Tartaric acid (1).....	−·4147	−·3291	−·3719	·0856	·2302	3·079	2·408	2·744	·671	·2445	149·64	139·45	8·95 x=23·05	8·34=21·48	1·129
Gallic acid (2)	.....	−·0886	−·1014	·0446	·4398	1·403	0·900	1·152	·314	·2726	169·59	191·99	12·60	14·27	1·035
Dextrin (2)	−1·1775	−·8245	−1·0010	·3530	·3527	48·142	35·409	41·776	12·773	·3048	323·24*	770·82	30·03	71·61	0·451
Amylodextrin (2) ...	−·0874	−·0620	−·0747	·0255	·3299	11·704	8·08	9·892	3·200	·3235	323·24*	2486·1	32·84	260·11	0·136
Tannin (1)	−·0781	−·0668	−·0724	·0113	·1561	5·177	4·167	4·672	1·010	·2162	331·22*	1219·6	15·48 x=39·90	57·01=146·91	0·286
„ (2)	−·1463	−·1185	−·1324	·0277	·2092	15·990	11·914	13·956	4·084	·2926	331·22*	1983·1	28·36	169·82	0·175
Cane-sugar (1)	−·3631	−·2981	−·3306	·0650	·1966	6·266	5·149	5·707	1·115	·1952	„	326·3	13·00 x=33·50	12·43=32·04	1·068
„ (2)	−1·3072	−·9333	−1·1203	·3739	·3338	21·588	15·674	18·631	5·914	·3174	341·2	314·32	34·38	31·67	1·142
„ (2)	−·8167	−·5945	−·7056	·2222	·3149	13·798	10·132	11·965	3·666	·3064	„	320·49	32·03	30·09	1·120
„ (2)	−·3881	−·2814	−·3348	·1067	·3187	6·638	4·837	5·737	1·801	·3139	„	323·87	33·63	31·92	1·109
„ (2)	−·1877	−·1295	−·1586	·0582	·3670	3·242	2·229	2·735	1·013	·3704	„	325·92	46·81	44·71	1·102
Maltose (2)	−·3388	−·2502	−·2945	·0886	·3009	6·377	4·789	5·583	1·588	·2844	341·2*	358 29	27·60	28·98	1·002
Raffinose (2)	−·3861	−·2862	−·3362	·0996	·2971	8·826	6·757	7·792	2·069	·2655	502·8*	428·04	35·45	30·88	1·208

TABLE II.—Supplementary Freezing-point Determinations.

Substance.	Parts to 100 of Water.	F.-p.	Substance.	Parts to 100 of Water.	F.-p.
Tartaric acid.....	2·152	—·2966°	Dextrin	27·484	—·6208°
Alloxan	1·425	—·2000	„	47·943	—1·1082
Glycerine	1·453	—·3023	Tannin	2·557	—·0440
Maltose	4·670	—·2463	„	12·310	—·1221
Pyrogallol	1·603	—·2228	„	15·804	—·1110
Gallic acid.....	0·667	—·0697	„	10·184	—·0844
„	0·133	—·0180	„	4·983	—·0542
Raffinose	0·640	—·2669	„	2·473	—·0342
Amylodextrin ...	7·940	—·0609			

The "molecular" depression, which, on the theory of osmotic pressure, will be proportional to mv^2, must, when we take the molecular weights calculated from it (m'), be an absolute constant, whereas the values for this same quantity ($m'v^2$), when deduced from the diffusion-experiments, and when these same molecular weights are used, are far from being constant; moreover, while the "theoretical" molecular weights give the values of mv^2 in the diffusion experiments with dextrin, amylodextrin, and tannin as being similar to those with the other substances investigated, they will, when used for calculating the molecular depression, give values from $\frac{1}{2}$ to $\frac{1}{8}$th only of those obtained with the other substances investigated. These values are given in the last column of the table: molec. dep. = (mean dep. × m) ÷ (mean strength × 17·96).

The fact that the results with dextrin, amylodextrin, and tannin are of doubtful accuracy must, it is true, weaken the strength of any conclusions based on them. But, on the other hand, the fact that they do not give exceptional values for mv^2 renders it probable that they are not very inaccurate; and, moreover, the exceptional values which they give for $m'v^2$ are not out of harmony with the results with the other substances; for the sugars, where the molecular weights are large, give values which are considerably larger than those given by the other substances examined. There seems indeed to be a general tendency for $m'v^2$ to increase with the molecular weight of the substance diffusing: thus, with the first seven substances entered in the table we have molecular

weights from 60 to 150, and the value of $m'v^2$ is generally about 20: with the last three substances in the table, where the molecular weights are high, 314 to 430 (taking the calculated values m'), $m'v^2$ is much larger, namely over 30; while dextrin, tannin, and amylodextrin show still larger, and, taken in their order, increasing molecular weights, and also larger and increasing values for $m'v^2$. Thus it would appear that with higher molecular weights the rate of diffusion is abnormally large.

The exceptionally large values for mv^2 in the case of the weakest solution of cane-sugar is remarkable, but in the absence of a duplicate determination it is well not to lay much stress upon it.

XVI. *Contact-Action and the Conservation of Energy.* *By* Prof. J. G. MacGregor, *M.A., Sc.D.**

SEVERAL years ago Prof. O. J. Lodge, in a series of papers published in this Magazine†, proposed new definitions of work done and energy, and claimed (1) that by their aid he had deduced from the third law of motion and the hypothesis of universal contact-action alone, a law (which he called *the* law) of the conservation of energy; (2) that the law thus deduced was an extension of, and fully as axiomatic as, the law ordinarily enunciated under the same name; (3) that action at a distance might be shown to be incompatible with Newton's third law, or the law of the conservation of energy, or both; and (4) that energy cannot be transferred without being transformed, or transformed without being transferred. These claims, though *primâ facie* so extraordinary as necessarily to have drawn attention, have never, so far as I am aware, been seriously challenged, and it is, perhaps, somewhat late in the day to challenge them now; but the remarkable progress which has recently been made in the application of contact-action theories, seems to make it desirable that they should be subjected to examination.

(1) *The Deduction of the Conservation of Energy.*

In the first version of the argument by which this deduction is made ‡, Prof. Lodge seems to me (*a*) to assume the ordinary law of the conservation of energy in addition to the third law

* Communicated by the Author.

† Phil. Mag. [5] vols. viii. (1879) p. 277, xi. (1881) pp. 36 & 529, xix. (1885) p. 482.

‡ Ibid. vol. viii. (1879) p. 278.

of motion and contact-action, and (*b*) to deduce, not a law of the conservation of energy, but of its conservation during transference merely.

(*a*) The unacknowledged assumption is made in the "definition" of energy :—"Whenever work is done upon a body, an effect is produced in it which is found to increase the working-power of that body (by an amount not greater than the work done) ; hence this effect is called energy, and it is measured by the quantity of work done in producing it. Whenever work is done by a body, *i. e.* anti-work done on it, its working-power is found to be diminished (to at least the extent of the work done), and it is said to have lost energy—the energy lost being measured, as before, by the anti-work done in destroying it." The words "is found" indicate an appeal to experience. We may readily recognize what it is, if we note that the increment or decrement of working-power which is produced in a body on or by which work has been done, may be kinetic or potential, and that, as Prof. Lodge says*, "for a body to possess kinetic energy you must have not merely motion, you must have a guarantee of persistence of motion, the body must possess inertia," and "for a body to possess potential energy we must have two things—the exertion of a force, together with a guarantee that that force shall be exerted over a certain distance ; *i. e.* a continuance of the force even after motion is permitted." If, then, these two guarantees be expressed quantitatively, so as to ensure the equality of the change of working-power to the work done, they will form a statement of the experience to which appeal is made. When so expressed, the former is seen to be Newton's second law of motion, and the latter the axiom that the work done by the mutual forces between the parts of a material system during any change of its configuration depends only on the initial and final configurations. If these guarantees cannot be deduced from the third law and universal contact-action, they are thus unacknowledged assumptions in the argument under consideration.

We may assume that Prof. Lodge will not hold it to be possible to make this deduction in the case of the latter of the two assumptions mentioned. He does hold, however, that Newton's second and third laws of motion are different aspects of one law †, and he may therefore regard the first of the two guarantees mentioned above as not forming an additional assumption in his argument. I have not access to 'The Engineer' of 1885, in which he says his argument in support

* Phil. Mag. [5] vol. xix. (1885) p. 485.

† Ibid. vol. xix. (1885) p. 483.

of this view is published. But in the edition of his book on Elementary Mechanics which bears the date 1892, he reaches this conclusion in the following way (p. 56) :—" It [Newton's third law] is deducible from the first law of motion (see Maxwell, 'Matter and Motion'), for if the forces exerted by two parts of the same body on each other were not equal and opposite, they would not be in equilibrium ; and consequently two parts of the same body might, by their mutual action, cause it to move with increasing velocity for ever, the possibility of which the first law denies. We have already shown that the first law is a special case of the second, and now we have deduced the third from the first ; hence all are really included in the second, which is therefore excessively important." That the first law is a special case of the second is obvious ; but that the third is deducible from the first in the above way I have elsewhere * endeavoured to disprove. It is not necessary to repeat the discussion here ; for it will probably be sufficient to point out that the equality and opposition of the action and reaction of two parts of the same body do not constitute the third law of motion, that law asserting the equality and opposition of the action and reaction between two bodies, to each of which the first law applies. That this criticism is sound becomes especially obvious if we reflect that the laws of motion, as fundamental hypotheses of dynamics, must be held to apply to particles, not to extended bodies ; and the above argument is clearly inapplicable to a particle.

The unacknowledged assumptions are thus not deducible, at least have not been deduced, from those admittedly used. Now the law of the conservation of energy, as ordinarily enunciated, may be deduced from these two assumptions alone. Hence, in the argument under consideration, Prof. Lodge assumes the ordinary law of the conservation of energy in addition to the third law of motion and universal contact-action.

(*b*) The following is the conclusion which he draws :—" Hence the energy gained by the first body is equal to the energy lost by the second ; or, on the whole, energy is neither produced nor destroyed, but is simply transferred from the second body to the first." This states only that energy is conserved during transference, and says nothing as to its fate after transference to the first body, and during residence

* In an Address on the fundamental hypotheses of Dynamics, read at the last Meeting of the Royal Society of Canada, and to be published in vol. x. of its Transactions. See abstract in 'Science,' vol. xx. (1892) p. 71.

in it. The law deduced is thus not a law of the conservation, but of the transference of energy. Obviously, with the assumptions which seem to me to have been employed, the complete law of conservation might have been deduced. But the conservation of energy during residence in the body could not have been proved without the explicit employment of the two assumptions involved in the definition of energy.

In a second version * of the above argument, Newton's third law and contact-action are the only assumptions made; but the conclusion drawn is not a law of the conservation of energy in the sense of working-power. The definition of energy in this argument is quite different from that of the earlier paper :—"Energy is that which a body loses when it does work; and it is to be measured as numerically equal to the work done." There is here no reference to working-power. Loss of energy is simply a synonym for work done by, and gain of energy for work done on. The conservation of energy which Prof. Lodge claims to have deduced is therefore the conservation of the work done on two bodies during mutual action, which is of the same nature as the conservation of their momentum, and is quite consistent with the non-conservation of their working-power.

(2) *Generality and Axiomatic Character of* Prof. Lodge's *Law.*

It will be obvious that, as Prof. Lodge's definition of energy is different from the ordinary definition, his law of conservation cannot be the same as that ordinarily enunciated under the same name. He says himself it is "probably a slight (very slight) extension" of the ordinary law †. We have seen, however, that in deducing it he assumes the ordinary law, the third law of motion and universal contact-action. It is therefore merely the form which the ordinary law takes in the particular case of contact-action with equal reaction.

This conclusion is borne out by a consideration of the definition of energy quoted above. Work done and the working-power of a body having been so defined ‡ as to make

* Phil. Mag. [5] vol. xix. (1885) p. 483.

† Ibid. vol. xi. (1881) p. 533.

‡ "Whenever a body exerting a force moves in the sense of the force it exerts, it is said to do work; and whenever a body exerting a force moves in the sense opposite to that of the force it exerts, it is said to have work done upon it, or to do anti-work, the quantity of the work being measured in each case by the product of the force into the distance moved through in its own direction." "The working-power of a body is measured by the average force it can exert, multiplied by the range or distance through which it can exert it." Ibid. vol. viii. (1879) p. 278.

their denotation identical with their ordinary denotation, provided the third law of motion hold, energy is defined qualitatively as being the working-power of a body, and quantitatively as being measured by the work done in producing it. The ordinary definition of energy is working-power simply, whether that power be possessed by a body or a system, its measure being the work the body or system can do. Prof. Lodge's energy will therefore be identical with energy in the ordinary sense only in cases in which his work done and his working-power are identical with ordinary work done and ordinary working-power, and in which the working-power of a system is the sum of the working-powers of the bodies of which it consists. Now this latter condition requires that the actions between the bodies of the system shall occur only at constant distance. For if the actions might occur at variable distance, a part of the working-power of the system would be potential working-power which could not be said to be possessed by the bodies singly. The former condition is satisfied if the third law of motion hold. Hence Prof. Lodge has so defined energy as to make its denotation identical with the ordinary denotation only in cases of action with equal reaction at constant distance.

Prof. Lodge asserts also that his law is "fully as axiomatic as" the ordinary law*. Mere assertion, however, cannot make two propositions equally axiomatic. They must be proved to be so. And the test is very simple. If they are applicable with equal generality in the investigation of dynamical phenomena, they are equally axiomatic; if not, they are not. Now, if there be actions in nature which are not actions at constant distance, Prof. Lodge's law is not applicable to them, while the ordinary law is. Even if it be admitted that all actions in nature are contact-actions, there are many groups of phenomena which, in the present state of our knowledge of them, cannot be investigated on the hypothesis of contact-action. The early stages of their investigation must be conducted by the aid of the fiction of action at a distance; and in such stages Prof. Lodge's law is not applicable, while the ordinary law is. Hence Prof. Lodge's law is not so general in its applicability as the ordinary law.

(3) *Deduction of Contact-Action.*

In Prof. Lodge's argument to prove the incompatibility of action at a distance with the third law of motion and the law of the conservation of energy †, he seeems to me neither to

* Phil. Mag. [5] vol. xi. (1881) p. 533.
† Ibid. vol. xi. (1881) p. 36.

assume a law of the conservation of working-power deduce contact-action.

The energy of which he assumes the conservation is (in the same way as in the second version of his deduction of the law of conservation:—A body "is said" to have lost or gained an amount of energy numerically equal to the work done by or on it respectively. There is no reference to working-power. What he assumes, therefore, is the conservation of the work done on two bodies during their mutual action.

The conclusion drawn is that "the two bodies must move over precisely the same distance in the same sense," which is action at constant distance, not contact-action. Nor does the assertion that they are "practically" the same make it contact-action.

It is obvious, however, that if the conclusion reached above is sound, viz., that Prof. Lodge's law of the conservation of energy is the ordinary law expressed for the particular case of action with equal reaction at constant distance, action at variable distance must be incompatible with it and the third law of motion.

The argument to show action at a distance to be incompatible with the law of the conservation of energy alone is as follows *:—"If it were possible for two bodies exerting stress on one another to move over unequal distances, then it would be possible to obtain work without the anti-work, and thus to get a new source of energy (technically called the perpetual motion); but, as a fact of experience, it is not possible." Clearly, in the case supposed, there would be a new source of energy as defined by Prof. Lodge. But a new source of energy as thus defined does not imply the perpetual motion. For in such a case there would be working-power which could not be called energy according to the definition; and the ordinary law of the conservation of energy tells us that, provided the stress supposed to act were independent of the velocities of the bodies acted upon, the change produced during the motion in this portion of the working-power of the system would be such as to render the perpetual motion impossible.

No attempt is made, in the papers cited above, to show action at a distance to be incompatible with Newton's third law of motion alone, although it is asserted † that the incompatibility may be proved.

* Phil. Mag. [5] vol. viii. (1879) p. 279.
† Ibid. vol. xi. (1881) p. 36.

(4) *Transference and Transformation of Energy.*

Prof. Lodge's argument to show that, on the assumption of contact-action, "energy cannot be transferred without being transformed," is as follows*:—"When a body possessing potential energy does work, its 'range' † necessarily diminishes, while the motion of the body on which the work is done increases. On the other hand, when a moving body does work its motion diminishes, and the body which resists the motion, since it yields over a certain distance, gains potential energy." It seems to me that these sentences would be equally accurate if we were to subject them to "double decomposition," after which process they would read thus:—When a body possessing potential energy does work its range necessarily diminishes, while the body on which work is done, since it yields over a certain distance, gains potential energy. On the other hand, when a moving body does work its motion diminishes, while the motion of the body on which the work is done increases.—A statement which would in general be more complete than either, would be obtained by combining the two. For if one body exert on another a certain force through a certain distance the same work is done on it, whether the former body lose kinetic or potential energy in doing the work; while the effect produced in the latter body will in general be a change both in its motion and its state of strain, *i. e.* both in its kinetic and its potential energy. Thus, whether the former lose kinetic or potential energy, or both, the latter will, in general, gain both, or transference of energy will, in general, involve partial but not complete transformation.

Prof. Lodge cites the air-gun as an instance of the transformation of potential into kinetic energy during transference. If we extract the bullet and plug up the muzzle it will serve equally well as an instance of the transference of potential energy without transformation. For if we now pull the trigger, the compressed air will do work on the air in the barrel. The "range" of the former will diminish, that of the latter will increase. As an instance of the transformation of kinetic into potential energy during transference, he selects the case of a bullet fired against a spring and caught by it. But if the spring have inertia, the energy acquired by it through the work done by the bullet must be partly kinetic, and in such a case, therefore, the transformation is only partial. Such instances, however, must be defective as illus-

* Phil. Mag. [5] vol. xix. (1885) p. 486.

† That is "the distance through which it can exert force."

trations, because the air, the spring, the bullet, which are treated as simple bodies, must be regarded as complex systems between the parts of which transferences of energy are occurring. When we make a more intimate study of such instances from the point of view of contact-action, we must, as Prof. Lodge points out, regard bodies as consisting of particles connected by a medium possessing some property of the nature of elasticity. If we assume the particles to be rigid they can, of course, have kinetic energy only. If the medium be assumed to have no inertia, its elements can have potential energy only. Hence if both assumptions be made, transference of energy between the particles and the medium must involve complete transformation, while transference from element to element of the medium must occur without transformation. If, however, both the particles and the medium be assumed to have both inertia and elasticity, the transference of energy will, in general, it seems to me, involve only partial transformation, whether it occur between the elements of the medium or between the particles and the medium. When, therefore, Prof. Lodge states that "a bullet fired upwards gradually transfers its undissipated energy to the gravitation medium, transforming it at the same time into potential," he seems to me to assume that the bullet is rigid and that the medium is without inertia.

Prof. Lodge states finally that "energy cannot be transformed without being transferred," but he gives no demonstration of this proposition. I find it difficult to reconcile with this statement one of his illustrations:—"A perfectly elastic bounding ball has all its energy transformed into potential at the middle of every period of contact with the obstacle from which it rebounds." Immediately after contact has ceased all its energy is kinetic, for apparently vibrations are excluded by hypothesis. The energy has thus been completely transformed without transference from the ball. It may, of course, be held that the ball must be regarded as a system of particles connected by an elastic medium. But in that case, what has been said of the ball, as a whole, is true of the particles in contact with the obstacle, if they are assumed to be elastic, or, if not, of the elements of the medium in contact with them, provided the medium be assumed to have inertia. After the middle of the period of contact, they do work on the elements of the medium beyond them. No work is done on them. They, therefore, lose energy and gain none. Yet after contact is over they possess kinetic energy. Whence has it come, if not through transformation of their own potential energy? That energy cannot be trans-

formed without being transferred must, of course, be true if bodies consist of particles with inertia but without elasticity, and if the medium connecting them possess elasticity but not inertia. Indeed, on these assumptions we may go farther and say it cannot be transformed without being transferred either from particles to medium, or from medium to particles. If, however, either or both be assumed to have both properties, the proposition seems to me to be erroneous, and certainly requires proof.

In concluding the discussion of this subject Prof. Lodge says:—"All I have stated is that change of form is necessary and universal whenever energy is transferred." If this is all the statements under discussion are to be taken to mean they may be admitted at once, on the assumption of contact-action. But this version of the statements quoted above seems to me to be a new statement altogether. For, expressed in terms of energy, it says merely that when one body does work on another through the exertion of contact-force the potential energies of both bodies in general undergo change.

Dalhousie College, Halifax, N.S.,
Dec. 30th, 1892.

XVII. *Experiments with High Frequency Electric Discharges.* *By* A. A. Campbell Swinton *.

THE writer has succeeded in passing through his body from hand to hand sufficient electricity to bring the filament of an ordinary 5-candle power 100-volt incandescent lamp very nearly to full incandescence, or to bring the filament of a 32-candle power 100-volt lamp to full redness. Practically no sensation was experienced.

The apparatus employed consisted of a large "Apps" induction-coil capable of giving 10-inch sparks, supplied with current through the ordinary vibrating contact-breaker, and a resistance consisting of eight 50-candle-power lamps in parallel, from a 105-volt continuous-current supply. The total energy in the primary, excluding what was lost in the resistance and contact-breaker, was about 350 watts, or not far off half an electric horse-power. To the positive and negative terminals of the secondary of the induction-coil were connected respectively the inside and outside coatings of three half-gallon Leyden jars, connected in parallel. The disruptive discharge of these jars across an air-gap of about a quarter of an inch excited the primary of a simple form of high-frequency coil similar to those employed by Mr. Tesla and

* Communicated by the Author.

Prof. Elihu Thompson. The secondary of this coil consisted of 500 turns of No. 26 S.W.G. cotton-covered wire wound on a paper tube. Outside this paper tube was a glass tube, upon which the primary, consisting of 10 turns of three No. 16 guttapercha-covered wires, in parallel, was wound. The whole coil was immersed in resin oil contained in a wooden trough. The ends of the secondary were connected through small glass tubes, also filled with oil, to brass balls.

On approaching the hand to one of the balls forming the terminals of the oil-coil, sparks shot out from the brush discharge which surrounds it. If the spark is taken on the skin a sharp prick is felt, but on approaching the terminal or touching it with a piece of metal grasped in the hand, or after grasping the terminal itself, practically no appreciable sensation is felt. If the terminal is grasped in this manner with the right hand, sparks will shoot out from the left hand or indeed from any portion of the body, if brought into proximity with another person, a piece of metal, the gas- or water-pipes, or any conducting body. In the experiment referred to the incandescent lamp was hung by one terminal on a wire connected to earth, and connexion was made between the other lamp terminal and the coil through the two arms and body by the right hand being brought into contact with one terminal of the oil-coil, and a piece of metal grasped in the left hand being approached to the free terminal of the lamp. At the first approach the bulb of the lamp became filled with phosphorescent light, but, on reducing the distance between the metal in the left hand and the free lamp terminal, sparks shot out between them and the filament at once became incandescent—the incandescence increasing very nearly to the full normal amount when the piece of metal and the lamp terminal were finally brought into contact.

To produce a similar incandescence of the filament with continuous or alternating currents of ordinary frequency would require about one fifth of an ampere, and at first sight it would seem that this quantity of current must pass through the arms and body of the operator.

It has been generally assumed that with high-frequency currents the current is rendered harmless by reason of the high frequency—in fact, that high frequency renders harmless to the human body currents of a strength that would be dangerous and painful, if not fatal, were the frequency lower. The writer is inclined to think that another explanation is possible, and that the true fact is, not that high frequency renders harmless a given strength of current that with ordinary frequency would be harmful, but that with high frequency it is possible to obtain effects with exceedingly small currents,

that with continuous and ordinary alternating currents can only be obtained by the use of much larger currents.

This hypothesis is probably applicable to many other high-frequency effects, but as applied to the above-mentioned experiment it is simply this:—The lamp-filament having a certain definite resistance, with continuous or ordinary alternating currents which pass uniformly or nearly so through the section of the filament, a certain amperage of current is necessary to produce the number of watts required to raise the filament to incandescence. With the high-frequency currents, on the other hand, as is well understood, the current travels chiefly on the outer surface of the filament, little or none passing through the central portion. The current is in fact merely skin-deep. The virtual resistance is therefore very high, as only an extremely small portion of the sectional area of the filament acts as a conductor. There is an ample sufficiency of volts, and though the current is very minute there is a sufficient expenditure of watts to raise the filament to incandescence. The lamp, in fact, ceases to be a 100-volt lamp and becomes, it may well be, a 100,000-volt lamp. As confirming this hypothesis, it should be mentioned that while the filament was incandescent sparks passed between the lamp terminals, which were at some distance apart, this being evidence that there was a difference of potential amounting at least to thousands of volts between the two ends of the filament.

Returning to the experiments, several other curious results were obtained. If, instead of connecting the lamp to the coil through the human frame, a wire was used, the filament became much brighter than in the previous experiment; in fact, it gave considerably more than its normal candle-power. From this it was evident that the human body offered considerable opposition of some description to the passage of the electricity. In order to form some idea of the amount of this opposition, the body was again inserted in the circuit between the coil and the lamp, as previously, and the thumbs of the two hands brought near together. Sparks about one quarter of an inch in length were found to pass between them, evidencing that the two hands of the operator had a difference of potential between them apparently equal to some thousands of volts. When the sparks passed between the hands, or when the wrists were brought into contact, so as to short-circuit, as it were, to some extent the resistance of the arms and body, the filament became very appreciably brighter. It should be mentioned that when the sparks were allowed to pass between the hands very perceptible shocks were felt in the wrists.

Another experiment was to connect one lamp terminal by a wire to the coil, connect the other lamp terminal to earth, and short-circuit the lamp through the body by grasping the coil terminal with one hand and a piece of metal connected to earth with the other. The effect of so doing was to reduce the incandescence of the filament to rather less than one half its normal amount, half of the available current going apparently through the lamp, the other half through the body.

With the lamp terminal connected to the coil, it was found unnecessary to connect the other lamp terminal to earth to produce incandescence, all that was necessary being to touch this lamp terminal with a piece of metal held in the hand. That the incandescence of the filament produced under these conditions was due to the electrostatic capacity of the operator and not to his forming a connexion to earth, was evidenced by the fact that it made no perceptible difference whether he stood on the floor or on an insulated stool.

In all the above experiments the second terminal of the oil-coil was free and not connected to anything. It was, however, found that the effect of a second operator touching this terminal, or of connecting it by wire to earth, was to diminish the incandescence of the lamp-filament. It was also found that the filament incandesced to a greater degree of brightness when connected as above between one terminal of the coil and earth, than when it was directly connected between the two terminals of the coil, but that, while the operator experienced practically no sensation when his body was inserted between one terminal and earth, the sensation was very severe—in fact, quite unbearable—when the body was inserted between the two terminals. The above seem to show that capacity has much to do with the results obtained, and that the physiological effects of electric currents are not necessarily proportional to their heating-power.

It should also be mentioned that in some of the experiments there was a decided tendency for the filament to vibrate in unison with the contact-breaker of the induction-coil. In fact, in some cases the amplitude of vibration was sufficient to cause the end of the filament to beat against the glass of the lamp bulb.

XVIII. *Notices respecting New Books.*

Annals of British Geology, 1891. *By* J. F. Blake, *M.A.*, *F.G.S.* 8vo. Pages viii & 404. Dulau and Co., London, 1892.

In a review of the former volume (for 1890) in the Philosophical Magazine for March 1892, the plan of these "Annals" was fully described. It has been followed in the present volume, except

that:—no notice is taken of papers merely read before Societies, but not published in the year concerned,—the abstracts and Prof. Blake's notes thereon have been submitted to the authors, and those which have been received back are marked with an asterisk,—and a new feature is "the introduction of illustrations of all new British species, and of other important novelties."

On this last point we may observe that "the will may be taken for the deed"; but that, though inadequate in very many instances to define the characters of the intended fossils, the amateur outlines may serve as useful indications, to some extent, where the descriptive memoirs cannot be got at. The two maps (pls. i. and ii.), though roughly executed, seem to be more available for their intended purpose.

As the asterisk placed before the No. of an Article indicates that the abstract has been seen and corrected by the Author or Editor of its memoir, we may notice that fifteen articles are indicated in the Table of Corrections as being entitled to these asterisks, as well as the very many (the majority) of the abstracts standing in the text with those marks. Important corrections appear (from the List of Corrigenda) to have been fortunately made by the authors in some of these abstracts after the printing.

The "Personal Notes" of the former volume are now limited to critical footnotes. These are always suggestive, and not unfrequently decidedly useful.

Some of the articles are, relatively, of considerable length; for instance no. 6 (Murray and Renard) has 17 pages; no. 324 (A. S. Woodward) 7 pages; no. 334 (R. B. Newton) 9 pages. The "Personal Items" about the Staff and Officers of the Societies and Institutions are discontinued. The two Indexes (of Authors and Periodicals) are given, and one of *new names*. If the geographical and the geological points were indexed, we think advantages would accrue; and we venture to suggest that the cost of the plates might be saved to that end in the next volume.

The masterly (if not also *masterful*) manner in which the numerous memoirs are treated is well sustained, and tends always to indicate their interest, and often to advance their usefulness. Evidently no pains have been spared by the enthusiastic author in earnestly carrying out his plan of diffusing a correct knowledge of current British Geology, and of the work of British Geologists, among all who are interested in the Science.

XIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 76.]

November 23rd, 1892.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

THE following communications were read:—

1. "Outline of the Geological Features of Arabia Petræa and Palestine." By Prof. Edward Hull, LL.D., F.R.S., F.G.S.

The region may be considered as physically divisible into five

sections, viz. :—(i) The mountainous part of the Sinaitic Peninsula; (ii) the table-land of Badiet-el-Tîh and Central Palestine; (iii) the Jordan-Arabah valley; (iv) the table-land of Edom, Moab, and the volcanic district of Jaulân and Haurân; and (v) the maritime plain bordering the Mediterranean.

The most ancient rocks (of Archæan age) are found in the southern portion of the region; they consist of gneissose and schistose masses penetrated by numerous intrusive igneous rocks. They are succeeded by the Lower Carboniferous beds of the Sinaitic peninsula and Moabite table-land, consisting of bluish limestone with fossils, which have their counterparts chiefly in the Carboniferous Limestone of Belgium, and of a purple and reddish sandstone (called by the author 'the Desert Sandstone,' to distinguish it from the Nubian Sandstone of Cretaceous age), lying below the limestone. The Nubian Sandstone, separated from the Carboniferous by an enormous hiatus in the succession of the formations, is probably of Neocomian or Cenomanian age, and is succeeded by white and grey marls, and limestones with flint, with fossils of Turonian and Senonian ages. The Middle Eocene (Nummulitic Limestone) beds appear to follow on those of Cretaceous age without a discordance; but there is a real hiatus notwithstanding the apparent conformity, as shown by the complete change of fauna. In Philistia a calcareous sandstone in which no fossils have been observed is referred to the Upper Eocene; for the Miocene period was a continental one, when faulting and flexuring was taking place, and the main physical features were developed—*e. g.*, the formation of the Jordan-Arabah depression is referable to this period.

In Pliocene times a general depression of land took place to about 200–300 feet below the present sea-level, and littoral deposits were formed on the coasts and in the valleys. To this period belong the higher terraces of the Jordan-Arabah valley. The Pliocene deposits consist of shelly gravels. Later terraces were formed at the epoch of the glaciation of the Lebanon Mountains, when the rainfall was excessive in Palestine and Arabia.

The volcanoes of the Jaulân, Haurân, and Arabian Desert are considered to have been in active operation during the Miocene, Pliocene, and Pluvial periods; but the date of their final extinction has not been satisfactorily determined.

2. "The Base of the Keuper Formation in Devon." By the Rev. A. Irving, B.A., D.Sc., F.G.S.

In a paper published in the February number of the volume of the Quarterly Journal for the current year, the author definitely accepted the breccia which is clearly marked on the left bank of the Sid at Sidmouth as the base of the Keuper, but he had not then satisfactory data for determining a similar basement-line in the country between the valleys of the Sid and Otter, where the Keuper is repeated by the great Chit-rock Fault. Since then he has received information from the Rev. Dr. Dixon of Aylesbeare, mentioning the occurrence of breccia at several points on the east side of the Otter, and has subsequently visited the district, and with

Dr. Dixon traced the breccia (the true base of the Keuper) along the left bank of the Otter, which for many miles seems to mark the western limit of the Keuper in Devonshire.

As results, (i) the palæontological difficulty which the occurrence of *Hyperodapedon* east of Ottermouth presented is now removed; (ii) the statement made in the last paragraph on p. 71 of the author's paper in the February number of the Quarterly Journal needs some modification; (iii) the geological maps of the Devon area require considerable revision; (iv) data are furnished which enable us to estimate the thickness of the Upper Bunter at not more than about 100 feet; and (v) points of interest in the physiography of the country are indicated.

3. "The Marls and Clays of the Maltese Islands." By John H. Cooke, Esq., F.G.S.

The following deposits (in ascending order) occur in the Maltese Islands :—I. Limestone, II. *Globigerina*-limestone, III. Clays, IV. Greensands, V. Upper Coralline Limestone. The Marls and Clays forming the subject of this communication are No. III. of this list. They lie conformably upon the *Globigerina*-limestone, and so obscure is the line of demarcation between the two, and so striking the similarity of their fossils, that the Clay may be considered as an argillaceous division of the formation upon which it rests. The upper part of the *Globigerina*-limestone is referred to the Hornerschichten of the Vienna basin, and the Clay to the Schlier. The separation between the clay and the greensands is sometimes, though not always, complete, and occasionally the greensands are absent, and the coralline limestone rests directly on the clay. The thickness assigned to the clay by Dr. Murray (20 feet) is probably not far wide of the mark. A description of the lithological characters of the deposits of the clay division, based on microscopic evidence, is given. They consist largely of tests of foraminifera and minute fragments of minerals, and contain nodules of ochreous clay. A list of fossils of the clays is appended, including an addition of 31 species of foraminifera to the 122 contained in Dr. Murray's list.

December 7th.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read :—

1. "Note on the Nufenen-stock (Lepontine Alps)." By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S.

In 1889 the author was obliged to leave some work incomplete in this rather out-of-the-way portion of the Lepontine Alps. In the summer of 1891 he returned thither in company with Mr. J. Eccles, F.G.S., and the present note is supplementary to the former paper. The Nufenen-stock was traversed from north to south, and a return section made roughly along the eastern bank of the Gries Glacier. Gneiss abounds on the north side of the Nufenen Pass, followed by rauchwacke and some Jurassic rock. On the flank of the mountain are small outcrops of rauchwacke and of the so-called 'Disthene-

schists' (both badly exposed), followed by much Dark-mica schist, often containing black garnets. Higher up is a considerable mass of Jurassic rock with the 'knots' and 'prisms' which have been mistaken for garnets and staurolites, but Dark-mica schists set in again before the summit is reached. They continue down the southern flank of the peak; but rather north of the lowest part of the watershed, between Switzerland and Italy, the 'Disthene-schist' is again found, followed by a fair-sized mass of rauchwacke.

The return section gave a similar association in reverse order; and both confirmed the conclusions expressed by the author in 1890 as to the absence of garnets and staurolites from Jurassic rocks (with belemnites &c.), and the great break between these or the underlying rauchwacke (where it occurs) and the crystalline schists, in which garnets often abound, of the Lepontine Alps. The crystalline schists and the Mesozoic rocks are thrown into a series of very sharp folds, which, locally, presents at first sight the appearance of interstratification.

2. "On some Schistose 'Greenstones' and allied Hornblendic Schists from the Pennine Alps, as illustrative of the Effects of Pressure-Metamorphism." By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S.

The author describes the results of study in the field and with the microscope of (*a*) some thin dykes in the calc-schist group, much modified by pressure; (*b*) some larger masses of green schist which appear to be closely associated with the dykes; (*c*) some other pressure-modified greenstone dykes of greater thickness than the first. The specimens were obtained, for the most part, either near Saas Fee or in the Binnenthal.

These results, in his opinion, justified the following conclusions:—

(1) That basic intrusive rocks, presumably once dolerites or basalts, can be converted into foliated, possibly even slightly banded, schists, in which no recognizable trace of the original structure remains.

(2) That in an early (possibly the first) stage of the process the primary constituents of the rock-mass are crushed or sheared, and thus their fragments frequently assume a somewhat 'streaky' order; that is to say, the rock passes more or less into the 'mylonitic' condition.

(3) That next (probably owing to the action of water under great pressure) certain of the constituents are decomposed or dissolved.

(4) That, in consequence of this, when the pressure is sufficiently diminished, a new group of minerals is formed (though in some cases original fragments may serve as nuclei).

(5) That of the more important constituents hornblende is the first to form, closely followed, if not accompanied, by epidote; next comes biotite (the growth of which often suggests that by this time the pressure is ceasing to be definite in direction), and lastly a water-clear mineral, probably a felspar, perhaps sometimes quartz.

(6) That in all these cases the hornblende occurs either in very elongated prisms or in actual needles.

The author brings forward a number of other instances to show that this form of hornblende may be regarded as indicative of dynamometamorphism; so that rocks where that mineral is more granular in shape (cases where actinolite or tremolite appears as a mere fringe being excepted) have not been subjected to this process.

3. "On a Secondary Development of Biotite and of Hornblende in Crystalline Schists from the Binnenthal." By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S.

Both the rocks described in this communication come from the Binnenthal, and were obtained by Mr. J. Eccles, F.G.S., in the summer of 1891. They belong to the Dark-mica schists described by the author in former papers, and have been greatly affected by pressure. In each a mineral above the usual size has been subsequently developed. In the rock from near Binn this mineral is a biotite; the dimensions of one crystal, irregular in outline and having its basal cleavage roughly perpendicular to the lines indicative of pressure, are about ·175 × ·03 inch. The other mineral, from the peak of the Hohsandhorn, is a rather irregularly formed hornblende, the crystals (which lie in various directions) being sometimes more than half an inch long. The exterior often is closely associated with little flakes of biotite. The author discusses the bearing of this fact, and the circumstances which may have favoured the formation of minerals, so far as his experience goes, of an exceptional size.

Some remarks also are made on the relation of these structures developed in the Alpine schists to the various movements by which those rocks have been affected, and on the general question of pressure as an agent of metamorphism.

4. "Geological Notes on the Bridgewater District in Eastern Ontario." By J. H. Collins, Esq., F.G.S.

The plateau of the Bridgewater district consists chiefly of gneiss and mica-schist, with subordinate beds of white marble, quartz-conglomerate and quartzite, and some veins of 'giant-granite.' The general dip of the gneissose series is eastward.

The author notes the effect of frost in splitting off flakes of the gneissose rocks and conglomerates, especially on the bare glaciated surfaces, and suggests that many of the smaller and shallower lakelets may have originated by this process.

The conglomerates are described as gneisses and mica-schists, with subordinate pebble-beds.

The occurrence of gold in quartz-veins near Flinders and at Madoc is noted; and amongst other economic products are the micas of the granites, asbestiform actinolite, and marble. The author discusses the mode of origin of the granite, marble, and actinolite-rock.

XX. *Intelligence and Miscellaneous Articles.*

VISIBLE REPRESENTATION OF THE EQUIPOTENTIAL LINES IN PLATES TRAVERSED BY CURRENTS; EXPLANATION OF HALL'S PHENOMENON. BY E. LOMMEL. (Preliminary Notice.)

SIMPLE consideration shows that the equipotential lines at right angles to the lines of flow in a plate are at the same time the magnetic lines of force belonging to the flow. If iron filings are strewed on the plate with a sufficiently strong current, they arrange themselves to form a beautiful image of the equipotential lines.

If the plate is brought into a magnetic field these magnetic lines of force alter their position, and therefore also the lines of force which necessarily are at right angles to them. In this lies the simple explanation of Hall's phenomenon.—Wiedemann's *Annalen*, No. 12, 1892.

ON THE ACTION OF LIGHT UPON ELECTRICAL DISCHARGES IN VARIOUS GASES. BY F. BREISSIG.

As source of light the author used a gas-flame. As he had the intention of determining the influence of the visible rays in electrical discharges, he tried to find a gas in which this action is as great as possible, but he came to the conclusion that the difference between various gases in this respect is too small to lead to the preference of any one in particular.

M. Breissig uses Hallwachs' form of the luminous discharge with a somewhat different arrangement. Opposite the source of light is placed an amalgamated zinc plate, and in front of it a wire gauze, also amalgamated, of galvanized iron, both being insulated. The zinc plate was kept at constant potential by a Daniell's battery of 80 elements, while the wire gauze was connected with one quadrant pair of an electrometer. The potential was measured of the quantity of electricity passing from the zinc plate to the wire gauze owing to illumination.

A decrease of sensitiveness of the plate with the duration of the illumination was observed, as Hallwachs and Righi had also observed for other sources of light; moreover, an increase was observed in all the gases investigated as the pressure diminished. In opposition to the observations of others, the author found a feebler discharge in carbonic acid than in air; the deflexions are reduced to about one half: this phenomenon is due to the fact that in his experiments the rays of a spectral region are used differing from that of other observers, and the action of the various parts of the spectrum on many gases may be different. With cool gas a feebler action is observed if the gas has already been illuminated.

The discharges in some vapours were stronger than in all the gases examined, especially in air half saturated with alcohol vapour. The following table gives in round numbers the results observed by the author.

	Discharge.	
	Normal pressure.	Diminished pressure.
Atmospheric air	10	18–22
Oxygen	14	20
Hydrogen	8	16
Carbonic acid	6	14
Coal-gas	7	12
Sulphuretted Hydrogen	3	
Air containing vapour of		
Alcohol	30–40	about 70
Ether	20–30	„ 50
Turpentine	6	
Benzole	10–20	
Petroleum spirit	10	
Xylol	6	

In this the mean strength of the discharge in dry atmospheric air is taken at 10—*Inaugural Dissertation*, Bonn, 1891 ; *Beiblätter der Physik*, vol. xvii. p. 60.

NOTICE OF A METEORIC STONE SEEN TO FALL AT BATH, SOUTH DAKOTA. BY A. E. FOOTE.

On the 29th day of August, 1892, about 4 o'clock in the afternoon, while Mr. Lawrence Freeman and his son were stacking upon his farm two miles south of Bath, they were alarmed by a series of heavy explosions. On looking up they saw a meteoric stone flying through the air followed by a cloud of smoke. Its course was easily traced to the point where it fell within about twenty rods from where they were standing. The stone penetrated the hardened prairie to a depth of about sixteen inches, and when reached it was found to be so warm that gloves had to be used in handling it. Three small pieces of an ounce or two each had apparently been blown off by the explosions, but the stone still weighed 46¾ lb. One of these small pieces was found by some men not far distant, and was broken up and distributed among them. The explosions were plainly heard by a large number of people at Bath, two miles away, and at Aberdeen, nine miles away, it sounded like distant cannonading. The exterior of the stone presents the usual smooth black crust. The interior is quite close-grained, resembling in texture the stones from Möcs. The iron is abundantly disseminated through the mass ; and although the grains are small, they are easily distinguished and separated on pulverizing.

Preliminary tests made by Mr. Amos P. Brown, of the Mineralogical Department of the University of Pennsylvania, prove the presence of nickel and cobalt in considerable quantity.—*Silliman's Journal*, January 1893.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MARCH 1893.

XXI. *On the Equilibrium of Vis Viva.*—Part III. *By* Prof. LUDWIG BOLTZMANN*.

I think that a problem of such primary importance in molecular science ought to be scrutinized and examined on every side, so that as many persons as possible may be enabled to follow the demonstration.—*Maxwell, Scientific Papers,* ii. p. 713.

§ 1. *On the Variables which reduce the expression for the Vis Viva to a Sum of Squares.*

MAXWELL† was the first to establish the formula for the distribution of *vis viva* among monatomic gas molecules, which he regarded as perfectly hard spheres of similar or dissimilar form (mass and radius). He also worked out the case in which the molecules are considered as rigid bodies with three different moments of inertia, and he found that for such a gas the ratio of specific heats must be $1\frac{1}{3}$. Since, however, this ratio has the value 1·4 for the best known simple gases, he concluded that the mechanical analogy is at variance with known facts on this subject‡. It is remarkable that Maxwell, who was successful in presenting the solution of the problem with such almost inconceivable

* Communicated by the Author, from the *Sitzungsberichte der mathematisch-physikalischen Classe der königlich-bayerischen Akademie der Wissenschaften* (Munich), vol. xxii. part 3. Translated by James L. Howard, D.Sc.

† "Illustrations of the Dynamical Theory of Gases," Phil. Mag. January and June 1860, Sci. Pap. i. p. 377.

‡ Maxwell, Sci. Pap. i. p. 409.

ease, both in the case of spheres and of bodies which possess no axis of rotation, did not then think of considering the allied and almost similar case, namely that of the various perfectly smooth and rigid solids of revolution which differ from the spherical form. He would then have obtained exactly the desired value 1·4 for the ratio of specific heats.

The proof which Maxwell gave at that time for his law of distribution of kinetic energy was afterwards shown by himself to be insufficient; and in a second paper* he gave an exact proof that the distribution of *vis viva* found previously was a possible one, *i. e.* that when once set up among the molecules of the gas it would not be altered by their impact.

This proof as well as Maxwell's law itself is capable of considerable extension, and he pointed out its very close connexion with a far more general theorem which applies to any system in which any forces operate†. In the attempt to make this latter theorem still more general, however, Maxwell‡ committed an error in assuming that by choosing suitable coordinates the expression for the *vis viva* could always be made to contain only the squares of the momenta, this assumption being, as Lord Kelvin has shown §, in general incorrect. But the mistake may be easily corrected by a slight modification of Maxwell's conclusions. To demonstrate this let us turn to Maxwell's paper just quoted above, and write with him (Sci. Pap. ii. p. 720) $b_1, b_2, b_3 \ldots b_n$ for generalized coordinates, and $a_1, a_2 \ldots a_n$ as the corresponding momenta. We must then stop at Maxwell's equation (42) (*l. c.* p. 724), and so write for the *vis viva*

$$T = \tfrac{1}{2}[11]a_1^2 + [12]a_1 a_2 \ldots .$$

All Maxwell's conclusions as far as equation (29) inclusive are perfectly accurate. In order to correct the further conclusions we might write the following deduction in place of that of Maxwell, from that point onward. Let us suppose α to be a linear function of the momentum a, and thus write

$$\alpha_h = \sum_{k=1}^{k=n} c_{hk} a_k.$$

Then we can always choose the coefficients c so that (1) their

* Phil. Mag. [4] vol. xxxv. (1868); Sci. Pap. ii. p. 26.

† Boltzmann, *Wiener Sitzungsberichte*, vols. lviii., lxiii., lxvi., lxxii, lxxiv., lxxv.

‡ "On Boltzmann's Theorem on the Average Distribution of Energy," Camb. Phil. Trans. xii. part 3 (1878); Sci. Pap. ii. p. 713.

§ 'Nature,' 13th August, 1891.

determinant Θ is equal to unity, that is

$$\Theta = \begin{vmatrix} c_{11} & c_{12} & \cdots \\ c_{21} & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} = 1,$$

and (2) the doubled kinetic energy takes the form

$$2\mathrm{T} = \sum_{i=1}^{i=n} \mu_i \alpha_i^2.$$

In this investigation the coefficients c and μ are functions of the generalized coordinates $b_1 \ldots b_n$, but the α's cannot in general be regarded as momenta which belong to any system of generalized coordinates whatever. I will therefore call them "momentoids" in order to prevent confusion.

The angular velocities about the three principal axes of inertia of a solid in the most general case of rotation furnish an example.

I shall denote by $\frac{1}{2}\mu_i\alpha_i^2$ that portion of the whole *vis viva* which belongs to the momentoid α_i. Since $\Theta = 1$, we have $da_1, da_2 \ldots da_n = d\alpha_1, d\alpha_2 \ldots d\alpha_n$. Let us insert the variable T in place of a_1 on the left and of α_1 on the right, then

$$\frac{1}{\frac{d\mathrm{T}}{da_1}} d\mathrm{T}\, da_2\, da_3 \ldots da_n = \frac{1}{\frac{d\mathrm{T}}{d\alpha_1}} d\mathrm{T}\, d\alpha_2\, d\alpha_3 \ldots d\alpha_n.$$

Dividing by $d\mathrm{T}$ and observing that

$$\frac{d\mathrm{T}}{da_1} = \dot{b}_1, \quad \frac{d\mathrm{T}}{d\alpha_1} = \mu_1 \alpha_1,$$

we obtain

$$\frac{1}{\dot{b}_1} da_2\, da_3 \ldots da_n = \frac{1}{\mu_1\alpha_1} d\alpha_2\, d\alpha_3 \ldots d\alpha_n.$$

From Maxwell's equation (28) (*l. c.* p. 721) we find for the number of systems whose generalized coordinates lie between the limits b_1 and $b_1 + db_1 \ldots b_n$ and $b_n + db_n$, and whose momentoids lie between α_2 and $\alpha_2 + d\alpha_2 \ldots \alpha_n$ and $\alpha_n + d\alpha_n$ (α_1 being determined from the equation of *vis viva*) the value

$$\frac{\mathrm{NC}}{\mu_1\alpha_1} db_1 \ldots db_n\, d\alpha_2 \ldots d\alpha_n.$$

If we now proceed with the integration exactly as Maxwell does, we arrive at his equation (45), which is thus perfectly correct.

By calculating the probability that the *vis viva* $\frac{1}{2}\mu_n\alpha_n^2$

belonging to the momentoid α_n lies between the values k_n and $k_n + dk_n$, we again arrive exactly at Maxwell's expression (51) (*l. c.* p. 725).

The expressions (52) and (53) (*l. c.* p. 726) of Maxwell's paper thus represent the mean and maximum values of the *vis viva* belonging to any momentoid. Instead of the law of Maxwell that the mean *vis viva* has the same value for every coordinate, we now obtain the law that the mean value of the *vis viva* belonging to all momentoids is the same.

Since the number of momentoids is always the same as that of the degrees of freedom, the law given by Maxwell at the commencement of his paper (*l. c.* p. 716) still remains true, viz. that the mean kinetic energies of two given parts of the system are in the ratio of their respective degrees of freedom. The kinetic energy T_k of any portion whatever may therefore contain the products of different p_k's, the terms p_k being the momenta of the general coordinates of that portion. But T_k must not contain the product of a term p_k and another momentum which is not included among the terms p_k. As a special case, the law will apply without any modification to so-called polyatomic molecules of a gas, whose condition is expressible by generalized coordinates.

As $2\frac{\partial T}{\partial b}$ is equal to $\sum_{i=1}^{i=n} \alpha_i^2 \frac{\partial \mu}{\partial b}$ in all cases, my proof of the second law* will still be correct, provided that by q_h we understand, not the momenta belonging to the coordinates p_h, but the momentoids.

On the Special Cases suggested by Lord Kelvin as Test-cases.

§ 2. *Motion of a Material Point in a Plane.*

I believe that with these modifications Maxwell's proof of the laws enunciated in the previous paragraphs is a satisfactory one; but in addition I have already given another proof from a quite different point of view†. I believe therefore that its truth as a law of analytical mechanics can hardly be called into question‡. As I myself arrived at my theorem only

* Borchard-Kronecker's *Journal*, vol. c. p. 201 (1885).

† "On the Equilibrium of Heat between Polyatomic Gas-molecules. Part I. Motion of the Atoms in the Molecules," *Wien. Sitz.-Ber.* vol. iii. 9th March, 1871. "Some General Theorems on Equilibrium of Heat," *ibid.* 13th April, 1871. In the latter paper I first made use of generalized coordinates.

‡ It is an entirely different question, whether such systems present a sufficiently close analogy with hot bodies. This question cannot be discussed here; *cf.*, however, *Beibl.* v. p. 403 (1881).

after a laborious consideration of many special cases*, I can appreciate the value of continually testing general theorems by means of special examples, and will therefore take up one of the particular cases suggested as a test-case by Lord Kelvin, namely the one he mentions last; because it is the simplest, and because I respect the sentence of De Morgan, quoted once by Prof. Tait, to the effect that "formulæ, if too long, are often not read."

Let a material point of unit mass move in the plane of x, y. Let x, y be its coordinates, q its velocity, u, v the components of the velocity in the directions of the axes of coordinates, and θ the angle which the direction of motion makes with the positive direction of the axis of abscissæ, the angle being counted from 0 to 2π. Suppose the potential V to be any function of the coordinates. We assume that the motion neither becomes infinite nor asymptotically approaches a fixed limit; and that all possible sets of values of x, y, and θ which are consistent with the equation of *vis viva* are obtained with any required degree of approximation, provided the motion continues for a sufficiently long time T.

Let us take a z-coordinate perpendicular to the plane of x, y, and define any condition of the moving point by marking off as z-coordinate over the point where it happens to be, the angle θ which its velocity makes with the positive direction of abscissæ. We shall call the point of space with the coordinates x, y, θ the point which characterizes the condition of the moving body, or briefly the instantaneous condition-point.

We can then define our assumption thus:—In the course of an interval of time T the condition-point occupies all positions in a finite cylinder (the condition-cylinder) which has a height 2π in the direction of the axis of z. The condition-point passes suddenly from the base to the summit of this cylinder, and *vice versâ*; with this exception its motion is continuous.

Suppose the moving point to be at the point x, y at any time t, and let its velocity make an angle θ with the axis of abscissæ and have the components u, v. The condition-point at time t will then be a point A of space with coordinates x, y, θ.

After the lapse of a very short time δt, that is at time $t + \delta t$, let the moving point be at x', y'. Let θ' be the angle between the direction of motion and the axis of abscissæ, and u', v' the

* "On the Equilibrium of *Vis Viva*," *Wien. Sitz.-Ber.* vol. lviii. 8th October 1868.—"Solution of a Mechanical Problem," *ibid.* 17th December, 1868.—"Some General Theorems on Equilibrium of Heat" (end of part 2) (*l. c.*).—"Remarks on some Problems in the Mechanical Theory of Heat," *Wien. Sitz.-Ber.* vol. lxxv. 11th January, 1877 (end of part 3).

components of the velocity resolved along the coordinate axes.

We may denote the position of the condition-point at time $t+\delta t$ by A′. A′ will be called the point corresponding to A. If we consider δt as constant, every point within the condition-cylinder will possess its corresponding point. Always, when at any time the condition-point has occupied any point of space, it will, after a time δt has elapsed, pass to the corresponding point; and *vice versâ*, the moving body can never reach the corresponding point except by having passed through the point to which it corresponds at a time δt previously.

We have then

$$\left.\begin{aligned} x' &= x + q\cos\theta\,.\,\delta t, \quad y' = y + q\sin\theta\,.\,\delta t, \\ u' &= u + \xi\,.\,\delta t, \quad v' = v + \eta\,.\,\delta t, \end{aligned}\right\} \quad . \quad . \quad (1)$$

in which $\xi = -\dfrac{\partial V}{\partial x}$, $\eta = -\dfrac{\partial V}{\partial y}$ are the components of the force acting on the moving particle, and are therefore functions of x and y. Further,

$$\theta' = \operatorname{arctg}\frac{v'}{u'},$$

which gives, on substituting the above values,

$$\theta' = \theta + (\eta\,.\cos\theta - \xi\sin\theta)\,\frac{\delta t}{q}. \quad . \quad . \quad . \quad (2)$$

Now let us construct an infinitely small rectangular parallelopiped $dx\,dy\,d\theta$, of which one edge is situated at the point A. Let the fraction of the whole time T during which the condition-point lies within the parallelopiped be dt. This is the time during which the three variables x, y, θ will be included between the values x and $x+dx$, y and $y+dy$, and θ and $\theta+d\theta$. We may then write in all cases

$$dt = f(x, y, \theta)\,dx\,dy\,d\theta. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now construct at each point of the parallelopiped $dx\,dy\,d\theta$ the corresponding point, and hence obtain the parallelopiped $dx'\,dy'\,d\theta'$. That fraction of the time T during which the condition-point lies within $dx'\,dy'\,d\theta'$ is, according to equation (3),

$$dt' = f(x', y', \theta')\,dx'\,dy'\,d\theta'.$$

Since, however, according to our definition of the condition-point, every time it enters the parallelopiped $dx\,dy\,d\theta$ it must after an interval δt enter $dx'\,dy'\,d\theta'$, and since the interval

between the exits from the two parallelopipeds is also exactly δt, it follows that the condition-point must enter both parallelopipeds the same number of times and must remain for the same time in each. This gives $dt' = dt$, or

$$f(x', y', \theta')\, dx'\, dy'\, d\theta' = f(x, y, \theta)\, dx\, dy\, d\theta.$$

But we have

$$dx'\, dy'\, d\theta' = \begin{vmatrix} \frac{\partial x'}{\partial x}, & \frac{\partial x'}{\partial y}, & \frac{\partial x'}{\partial \theta} \\ \frac{\partial y'}{\partial x}, & \frac{\partial y'}{dy}, & \frac{\partial y'}{\partial \theta} \\ \frac{\partial \theta'}{\partial x}, & \frac{\partial \theta'}{\partial y}, & \frac{\partial \theta'}{\partial \theta} \end{vmatrix} . dx\, dy\, d\theta.$$

As δt is constant, and $q^2 = \text{const.} - 2V$, equations (1) and (2) give

$$\frac{\partial x'}{\partial x} = 1 + \xi \cos\theta \,.\, \frac{\delta t}{q}, \quad \frac{\partial y'}{\partial y} = 1 + \eta \sin\theta \,.\, \frac{\delta t}{q},$$

$$\frac{\partial \theta'}{\partial \theta} = 1 - (\xi \cos\theta + \eta \sin\theta)\, \frac{\partial t}{q}.$$

If we neglect the terms of order δt^2, the functional determinant reduces to

$$\frac{\partial x'}{\partial x} \cdot \frac{\partial y'}{dy} \cdot \frac{\partial \theta'}{\partial \theta} = 1,$$

and consequently

$$dx'\, dy'\, d\theta' = dx\, dy\, d\theta,$$

from which also $f(x', y', \theta') = f(x, y, \theta)$. As we can pass from the parallelopiped $dx\, dy\, d\theta$ to its corresponding one, and from this latter to its corresponding one, and so on, it follows that $f(x, y, \theta)$ is always constant, and therefore that $dt = \mathrm{C}\, dx\, dy\, d\theta$. This result agrees perfectly with that found in my paper previously quoted, on the "Solution of a Mechanical Problem."

Lord Kelvin denotes by $\mathrm{N}\, d\theta\, dr$ the number of times during the interval T that the moving particle traverses an element of surface, whose length in the direction of motion is ds and whose breadth perpendicular to this direction is dr, in such a manner that θ lies between the values θ and $\theta + d\theta$. As the moving point always remains for a time ds/q in the element of surface, the fraction of T during which the moving point is situated in $dr\, ds$ and has at the same time a direction of motion between θ and $\theta + d\theta$, is

$$\frac{\mathrm{N}}{q}\, dr\, ds\, d\theta.$$

But we have just seen that this time is

$$C\,dr\,ds\,d\theta,$$

from which it follows that $N = Cq$. N is therefore quite independent of the angle θ, and not only Lord Kelvin's coefficient A_1, but also A_2 and all the coefficients following vanish.

I can hardly doubt that Lord Kelvin will be satisfied with this result of his test-case.

§ 3. *On the Distribution of Kinetic Energy among* Kelvin's *Doublets.*

The other cases suggested by Lord Kelvin relate to a theorem which is closely connected with the problem just considered, but not by any means identical with it, nor even a special case of it; namely, the question of the equilibrium of heat in the case of polyatomic gaseous molecules. It can easily be shown that in this problem there exists one particular distribution of *vis viva* which is not altered either by internal motion of the molecules or by impacts.

Let $p_1, p_2, \ldots p_n$ be the generalized coordinates by which the positions of all constituents of a molecule are determined relatively to its centre of mass, the rotation of the molecule being included. Let $q_1, q_2, \ldots q_n$ be the corresponding momenta, T the total *vis viva* of the molecule, V the potential-function of its internal forces, u, v, w the components of the velocity of its centre of mass, and finally A and k constants; then the distribution of *vis viva* referred to is that in which the number of molecules per unit volume, for values of the variables $u, v, w, p_1, p_2, \ldots p_n, q_1, q_2, \ldots q_n$ between the limits u_1 and $u_1 + du_1, \ldots q_n$ and $q_n + dq_n$, is equal to

$$Ae^{-\kappa(V+T)}\,du \ldots dq_n.$$

If there are several kinds of molecules present the constant κ, but not A, must have the same value for each.

The verification of this result in the special case imagined by Lord Kelvin is so simple that I shall not consider it here. But the other proof, that the distribution of kinetic energy given by the above formula is the only possible one, can only be established indirectly by the assumption that a certain particular function must, if altered, be necessarily increased by collisions. As this function is very closely connected on the one hand with the quantity designated by Clausius as entropy*, and on the other hand with the probability of occurrence of

* *Wien. Sitz.-Ber.* Bd. lxxvi. (1877), Bd. lxxviii. (1878).

the state referred to, the second law of thermodynamics appears from it to be purely a law of probability.

It appears to me to be a matter of interest (*vide* Motto) to examine this latter proof for the case of the molecule provided with elastic springs as imagined by Lord Kelvin, and which, following his example, we shall call a "doublet." By a doublet let us understand the combination of two material points with masses m and m'', which attract each other with a force proportional to their distance apart. m'' (the nucleus) is never acted upon by any other force. The masses m (shells) of any two doublets impinge on each other like elastic spheres whenever they come within a distance D'' of each other. Besides these, suppose simple atoms of mass m' to be present, which collide with each other if they approach nearer than distance D', and with the shells if they come within distance D from them. We shall always write, for the sake of brevity, "shell" instead of centre of the shell, and "nucleus" instead of centre of the nucleus. Let x, y, z be the coordinates of the nucleus of a doublet referred to a system of rectangular coordinates the origin of which is at the centre of the shell and the axes of which have fixed directions; let u'', v'', w'' be the absolute components of the velocity of the nucleus, and $\mathfrak{u}, \mathfrak{v}, \mathfrak{w}$ the same components taken relatively to the shell; let g, h, k be the components of the velocity of the centre of gravity of the doublet, u, v, w those of the shell, and u_1, v_1, w_1 those of a single atom. Finally, suppose $\chi(x, y, z, \mathfrak{u}, \mathfrak{v}, \mathfrak{w}, g, h, k)\, dx \ldots dk$ to be the number of doublets per unit of volume for values of the variables $x \ldots k$ at the time t lying between the limits x and $x+dx \ldots k$ and $k+dk$, and let $f(u_1, v_1, w_1)\, du_1\, dv_1\, dw_1$ be the number of single atoms in unit of volume whose velocity-components u_1, v_1, w_1 lie between the limits

$$u_1 \text{ and } u_1+du_1, \quad v_1 \text{ and } v_1+dv_1, \quad w_1 \text{ and } w_1+dw_1.$$

Then the expression the value of which can only be diminished by impacts, and which for brevity we call the entropy, is

$$E = \int \chi \log \chi\, dx \ldots dk + \int f \log f\, du_1\, dv_1\, dw_1,$$

in which the integration extends over all possible values of the variables. The first term of the expression E can be obtained in the following manner. We write down the value of $\log \chi$ for every doublet contained in the unit of volume; *i. e.* we insert in $\log \chi$ for all the variables those values which it takes for the doublet under consideration. Then we add together all the values of $\log \chi$ so obtained. In order to

express this symbolically we may denote the sum by $\Sigma \log \chi$. In a similar manner the second term gives us $\Sigma \log f$, the summation being extended to all the single atoms in a unit of volume.

In order to prove that E can only diminish, let us first find the change produced in the value of $\Sigma \log \chi$ simply by the relative motion of nucleus and shell in the doublets, assuming no collisions to take place. In this case g, h, and k would obviously remain constant. On the other hand, we should have at any time t,

$$x = \mathrm{A} \sin (at + \mathrm{B}), \quad \mathfrak{u} = \mathrm{A}a \cos (at + \mathrm{B}),$$

and at time $t = 0$,

$$x_0 = \mathrm{A} \sin \mathrm{B}, \quad \mathfrak{u}_0 = \mathrm{A}a \cos \mathrm{B}.$$

If we consider all doublets for which A and B are included within specified infinitely close limits, then

$$dx\, d\mathfrak{u} = dx_0\, d\mathfrak{u}_0 = \mathrm{A}a\, d\mathrm{A}\, d\mathrm{B}\,; \quad . \quad . \quad . \quad . \quad (4)$$

and similarly for the y- and z-axes,

$$dy\, d\mathfrak{v} = dy_0\, d\mathfrak{v}_0, \quad dz\, d\mathfrak{w} = dz_0\, d\mathfrak{w}_0 \quad . \quad . \quad . \quad (5)$$

It can easily be shown that the equation

$$dx\, dy\, dz\, d\mathfrak{u}\, d\mathfrak{v}\, d\mathfrak{w} = dx_0\, dy_0\, dz_0\, d\mathfrak{u}_0\, d\mathfrak{v}_0\, d\mathfrak{w}_0$$

also holds good if the nucleus and shell have any other central motion whatever. (*Cf.* my investigation of the equilibrium of heat in the case of polyatomic gaseous molecules, previously referred to.) If no collisions were to take place the doublets, whose variables at time $t = 0$ lay between the limits x_0 and $x_0 + dx_0 \ldots k_0$ and $k_0 + dk_0$, would have their variables at time t between the limits x and $x + dx \ldots k$ and $k + dk$. Let us therefore consider for a moment the variable t as explicitly expressed in the function χ, in order not to exclude the possibility of a variation of χ with time. We have then as the number of the former doublets,

$$\chi(x_0 \ldots \mathfrak{w}_0, g, h, k, 0) dx_0 \ldots dk = \chi_0\, dx_0 \ldots dk$$

and of the latter

$$\chi(x \ldots k, t) dx \ldots dk = \chi dx \ldots dk.$$

Hence we have

$$\chi_0\, dx_0 \ldots dk = \chi\, dx \ldots dk,$$

and from (4) and (5)

$$\chi_0 = \chi,$$

from which it follows that

$$\chi_0 \log \chi_0,\, dx_0 \ldots dk = \chi \log \chi\, dx \ldots dk.$$

The integration of this last equation over all possible values of the variables involved in it shows us at once that the quantity $\Sigma \log \chi$ suffers no alteration by internal motion of the doublets, and the same will be true, of course, for any central motion. All that now remains is to determine the effect of the collisions.

Let us now introduce instead of $\mathfrak{u}, \mathfrak{v}, \mathfrak{w}, g, h, k$, the absolute velocities u, v, w, u'', v'', w''. Since

$$(m+m'')g = mu + m''u'', \quad \mathfrak{u} = u'' - u,$$

it follows that

$$dg\, d\mathfrak{u} = du\, du''.$$

If we write for the number of doublets in unit volume, whose variables $x, y, z, u'', v'', w'', u, v, w$, lie between the limits x and $x+dx \ldots w$ and $w+dw$, the value $\mathrm{F}(x, y, z, u'' v'', w'', u, v, w)\, dx \ldots dw$, where

$$\mathrm{F} = \chi\left(x, y, z, u'' - u \ldots \frac{mu + m''u''}{m+m''} \ldots\right),$$

then

$$\Sigma \log \chi = \int \mathrm{F} \log \mathrm{F}\, dx \ldots dw = \Sigma \log \mathrm{F},$$

in which the summation again extends to all the doublets contained in the unit of volume. Now denote by $\delta_1 \Sigma \log \mathrm{F}$ the increase in $\Sigma \log \mathrm{F}$ produced during time δt by the impact of doublets on each other, by $\delta_2 \Sigma \log f$ the increase in $\Sigma \log f$ during the same time, produced by the impact of single atoms on each other, and by $\delta_{12}(\Sigma \log \mathrm{F} + \Sigma \log f)$ the corresponding increase of the quantity in brackets, produced by the impact of doublets and single molecules.

To calculate $\delta_{12}(\Sigma \log \mathrm{F} + \Sigma \log f)$ we must sort out, from all the impacts between a shell and a single atom in unit volume during time δt, those collisions for which the velocity-components of the shell at the moment of the collision (and likewise before) lie between the limits u and $u+du$, v and $v+dv$, w and $w+dw$, the velocity-components of the nucleus being between u'' and $u''+du''$, v'' and $v''+dv''$, w'' and $w''+dw''$, the coordinates of the nucleus relatively to the shell being between x and $x+dx$, y and $y+dy$, z and $z+dz$; further, the velocity-components of the common centre of gravity of the shell and the single atom are to lie between p and $p+dp$, q and $q+dq$, r and $r+dr$, and the direction of the line of centres of the impinging atoms at the moment of impact are to lie within an infinitely narrow cone placed in a definite direction in space and having an infinitely small angle $d\lambda$. The velocity-components of the single atom at the instant when the impact

begins are then

$$u_1 = \frac{m+m'}{m'}p - \frac{m}{m'}u, \quad v_1 = \frac{m+m'}{m'}q - \frac{m}{m'}v,$$

$$w_1 = \frac{m+m'}{m'}r - \frac{m}{m'}w. \quad . \quad (6)$$

For the number of impacts which take place in unit volume during time δt, under the conditions specified above, we find without difficulty the value

$$dn = \mathrm{D}^2 . \mathrm{F}(x, y, z, u'', v'', w'', u, v, w) f(u_1, v_1, w_1)$$
$$\times \mathrm{V}\epsilon dx \ldots dw'' \, du \, dv \, dw \, du_1 \, dv_1 \, dw_1 \, d\lambda \, \delta t.$$

In this expression V is the relative velocity of the two atoms at the moment of collision, and ϵ the cosine of the acute angle between the line of motion and the line of centres. If we introduce instead of u_1, v_1, w_1 the variables p, q, r, from equation (6) we find

$$dn = \mathrm{D}^2 \mathrm{F} f_1 \frac{(m+m')^3}{m'^3} \mathrm{V}\epsilon \, dx \ldots dw'' \, du \, dv \, dw \, dp \, dq \, dr \, d\lambda \, \delta t,$$

in which the suffix 1 denotes that the values of the variables as given in equations (6) are to be substituted in the function.

In each of the impacts just specified a shell loses velocity-components u, v, w, and hence in all the dn impacts $\Sigma \log \mathrm{F}$ will be diminished by $dn \log \mathrm{F}$.

After each of the impacts considered let the velocity-components of the shell be between u' and $u' + du'$, v' and $v' + dv'$, w' and $w' + dw'$. In order that shells may be formed with these new velocities $\Sigma \log \mathrm{F}$ must be increased by $dn \log \mathrm{F}'$, where the affix denotes that the variables $x \ldots w''$, u', v', w' are to be substituted in the function F. We assume that the collisions are instantaneous, in which case the variables $x \ldots w''$ are unaltered by the impacts. The total increase of $\Sigma \log \mathrm{F}$ by reason of the impacts considered is, therefore,

$$dn (\log \mathrm{F}' - \log \mathrm{F}).$$

In like manner we find that $\Sigma \log f$ receives an increase

$$dn (\log f_1' - \log f_1)$$

during time δt from the same impacts, the affix and suffix meaning that the following values of the velocity-components of the impinging single atom after impact are to be substituted in the function f.

$$u_1' = \frac{m+m'}{m'}p - \frac{m}{m'}u', \quad v_1' = \frac{m+m'}{m'}q - \frac{m}{m'}v,$$

$$w_1' = \frac{m+m'}{m'}x - \frac{m}{m'}w. \quad . \quad (7)$$

The total increase of $\Sigma \log F + \Sigma \log f$ by all impacts of the type specified is, therefore, $dn\,(\log F' + \log f'_1 - \log F - \log f_1)$. From this we shall obtain the total increase previously designated by $\delta_{12}(\Sigma \log F + \Sigma \log f)$ if we integrate over all values of the variables whose differentials are contained in dn*.

This integration may be performed by means of a special device. In conjunction with the above terms which are furnished by the "specified" impacts, let us take the terms furnished by the "opposite" impacts, and thus divide the whole of the collisions into pairs.

We shall consider an impact to be "opposite" to any "specified" one when the condition of the colliding atoms at the end of either is exactly the same as their condition at the commencement of the other one. The centres of the colliding atoms must, however, be interchanged of course, since they approach each other before impact. The remaining variables $x \ldots w''$ will be included between the same limits for both impacts. In the accompanying figures the largest circle represents a shell, the smallest a nucleus, and the intermediate one a single atom; the arrows drawn through their centres represent

* If we assume that the second of the impinging atoms is not a single atom, but a shell, we arrive by exactly analogous reasoning at a similar equation

$$2\delta_1 \Sigma \log F = \int dn\,(\log F' + \log F_1' - \log F - \log F_1),$$

in which

$$F_1 = F(x_1, y_1, z_1, u_1'', v_1'', w_1'', u_1, v_1, w_1).$$

$$F_1' = F(x_1, y_1, z_1, u_1'', v_1'', w_1'', u_1', v_1', w_1').$$

u_1, v_1, w_1, and u_1', v_1', w_1' are the velocity-components of the second shell before and after the impact, and must be expressed by equations of similar form to (6) and (7). $x_1, y_1, z_1, u_1'', v_1'', w_1''$ are the remaining quantities by which the position of the second doublet at the moment of the impact is determined. Finally,

$$dn = D''^2 F F_1 V \epsilon\, dx \ldots dw''\, du\, dv\, dw\, dx_1 \ldots dw_1''\, dp\, dq\, dr\, d\lambda\, \delta t.$$

By similar processes of reasoning we should find

$$2\delta_2 \Sigma \log f = \int dn\,(\log f' + \log f_1' - \log f - \log f_1)$$

and

$$dn = D'^2 f f_1 V \epsilon\, du\, dv\, dw\, dp\, dq\, dr\, d\lambda\, \delta t.$$

The meanings of the quantities in these equations will be clear without further explanation.

the velocities. Figs. 1 and 2 show the configurations before and after an impact respectively, while figs. 3 and 4 give the

Fig. 1.

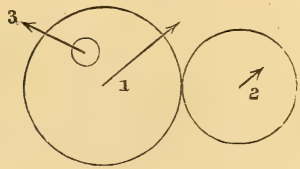


Fig. 2.

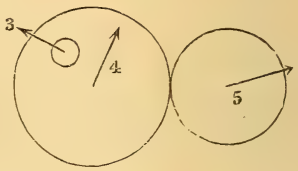


Fig. 3.

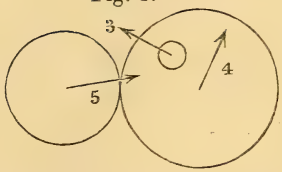
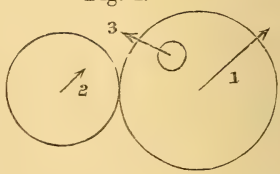


Fig. 4.



configurations before and after the corresponding "opposite" impact respectively. Arrows numbered alike have always equal lengths and make the same angle with the line of centres.

For all collisions which are "opposite" to those previously considered, the velocity-components of the impinging shell at the commencement of the impact lie between the limits

$$u' \text{ and } u'+du',\ v' \text{ and } v'+dv',\ w' \text{ and } w'+dw'$$

and at the end of the impact they lie between

$$u \text{ and } u+du,\ v \text{ and } v+dv,\ w \text{ and } w+dw.$$

The same holds good for the impinging single atom in which the motion of the centre of gravity, the magnitude of the relative velocity and its inclination to the line of centres have the same values for the opposite impact as for that originally considered. In each opposite impact a shell loses velocity-components u', v', w', and a single atom loses u_1', v_1', w_1'; on the other hand, a shell gains u, v, w, and a single atom u_1, v_1, w_1. If dn' is the number of collisions per unit volume in time δt which are opposite to those previously considered, the term $\Sigma \log \mathrm{F} + \Sigma \log f$ is increased by them to the extent of

$$dn' (\log \mathrm{F} + \log f_1 - \log \mathrm{F}' - \log f_1').$$

The total increase in the value of this expression due to the specified and opposite impacts together is

$$(\log \mathrm{F} + \log f_1 - \log \mathrm{F}' - \log f_1')(dn - dn').$$

If we integrate this expression for all values of the variables whose differentials are contained in du and du', we obtain

$2\delta_{12}(\Sigma \log F + \Sigma \log f)$, because we count every impact twice; once as a "specified," and the second time as an "opposite," impact. As V, ϵ, and $d\lambda$ are not changed by the impact, we have

$$dn' = D^2 F' f_1' \frac{(m+m')^3}{m'^3} V\epsilon\, dx \ldots dw''\, du'\, dv'\, dw'\, dp\, dq\, dr\, d\lambda\, \delta t.$$

It can easily be shown (most simply by a geometrical proof) that $du'\, dv'\, dw' = du\, dv\, dw$, and hence

$$\delta_{12}(\Sigma \log F + \Sigma \log f) = \frac{\delta t}{2} \int (\log F' + \log f_1' - \log F - \log f_1)$$

$$\times (Ff_1 - F'f_1') \frac{(m+m')^3}{m'^3} V\epsilon D^2 du\, dv\, dw\, dp\, dq\, dr\, dx \ldots dw''\, \delta\lambda. \quad (8)$$

Similarly it can be shown that

$$\delta_1 \Sigma \log F = 2\delta t \int (\log F' + \log F_1' - \log F - \log F_1)(FF_1 - F'F_1')$$
$$\times V\epsilon D'^2 dx \ldots dw''\, dx_1 \ldots dw_1''\, du\, dv\, dw\, dp\, dq\, dr\, d\lambda,$$

$$\delta_2 \Sigma \log f = 2\delta t \int (\log f' + \log f_1' - \log f - \log f_1)(ff_1 - f'f_1')$$
$$\times V\epsilon D'^2\, du\, dv\, dw\, dp\, dq\, dr\, d\lambda, \quad . \quad . \quad . \quad . \quad (9)$$

in which the variables are the same as in the footnote on page 165.

We shall confine our attention to the consideration of the stationary condition, in which F and f are at all times the same functions of the variables contained in them. In this case no causes except those already considered can effect changes in $\Sigma \log F$ and $\Sigma \log f$; and the total change in E during the time δt is therefore

$$\delta E = \delta_{12}(\Sigma \log F + \Sigma \log f) + \delta_1 \Sigma \log F + \delta_2 \Sigma \log f.$$

Since everything (and therefore E) remains unaltered, δE must be zero. But in the integrals of equations (8) and (9) the two factors in brackets have necessarily opposite signs, while the remaining quantities are essentially positive. The expression to be integrated is therefore necessarily negative, and the sum of the integrals of which δE is composed can only vanish if at each impact

$$F'f_1' = Ff_1, \quad F'F_1' = FF_1, \quad f'f_1' = ff_1. \quad . \quad . \quad . \quad (10)$$

Let us now consider the most simple case, namely, that in which the shells always pass each other without impinging, and similarly with the single atoms; but between a shell and a single atom let there be always an impact if they approach within distance D of each other. We have then only the first of the equations (10), but it holds good for every possible

impact. If we put the velocity of a single atom

$$\sqrt{u_1^2+v_1^2+w_1^2}$$

equal to c_1, then f_1 is clearly a function of c_1, but F may be expressed as a function of the following six variables:—(1) the two velocities c and c'' of shell and nucleus, (2) their distance apart ρ (measured from centre to centre), (3) the angles α and α'' which the directions of c and c'' make with the line ρ, the latter being supposed drawn from shell to nucleus, and (4) the angle β between the plane containing ρ and c and that containing ρ and c''.

Now imagine a collision to take place, and denote the values of these variables at the moment immediately before the impact by letters without an affix, their values just after the impact being distinguished by the affix. We can so choose the direction of the line of centres at the moment of impact and the direction of c_1, that c, α, and β take any required values c', α', and β', provided these latter furnish a real value c_1' of the variable c_1 after impact. This value will be determined by the equation of *vis viva*

$$m'c_1'^2+mc'^2=m'c_1^2+mc^2.$$

The values of the variables c'', ρ, and α'' will not be altered by the impact. The first of the equations (10) can therefore be written in the form

$$\mathrm{F}(c'', \alpha'', \rho, c, \alpha, \beta)\,.f_1(c_1)=\mathrm{F}(c'', \alpha'', \rho, c', \alpha', \beta')\,.$$
$$\times f_1\Big/\left(\sqrt{c_1^2+\frac{m}{m'}(c-c'^2)}\right).$$

This equation must be satisfied by all possible values of the variables c'', α'', ρ, c, α, β, c', α', β', and c_1; from which it follows easily that

$$f_1(c_1)=\mathrm{A}_1 e^{-\kappa m' c_1^2}, \quad \mathrm{F}=\mathrm{A}e^{-\kappa m c^2}.$$

in which A_1 and h are simple constants, while A may contain the variables c'', ρ, and α''.

It is therefore evident that the mean kinetic energies of a shell and a single atom are equal, and that Maxwell's law of distribution of velocities between shells and single atoms is satisfied, without assuming the existence of impacts of shells on each other, or of single atoms on each other. These assumptions do not alter the distribution of *vis viva* in the slightest degree, however, because the values of f_1 and F found above satisfy identically the other relations demanded by the equations (10). On the other hand, the condition that the nuclei should never come into collisions of any kind does not prevent the law from

applying even to them; but the proof of this is much more difficult. For, if such collisions existed, it would follow that F would depend upon c'' in exactly the same manner as it depends upon c, and there we should be forced to stop. In this case we must consider more closely the internal motion of the doublet.

We can next prove without difficulty that in the distribution of velocities just found the values of c, α, β are altered on the average in exactly the same manner and degree by each impact as by its opposite one, for every set of values of c'', ρ'', and α''. If, then, certain forms of central motion are suddenly destroyed by a collision, the same forms are produced again elsewhere equally often by other collisions, and consequently the same law of distribution of central motions would exist even if all impacts were suddenly to cease.

It is remarkable that just for the simple case imagined by Lord Kelvin, in which the central force is taken proportional to ρ, the calculation is exceedingly long. In order not entirely to forget the sentence of De Morgan, previously quoted, I will assume some other law, e. g. $a\rho + \frac{b}{\rho^3}$, or, indeed, any one in which the angle between two consecutive apsidal lines bears no rational proportion to π.

The total energy of a doublet is

$$L = \frac{mc^2}{2} + \frac{m''c''^2}{2} + \phi(\rho), \quad . \quad . \quad . \quad . \quad (11)$$

where ϕ is the potential-function. The doubled velocity of the relative motion of shell and nucleus in the plane of their central motion is

$$K = \rho\sqrt{c^2 \sin^2 \alpha + c''^2 \sin^2 \alpha'' - 2cc'' \sin \alpha \sin \alpha'' \cos \beta}, \quad . \quad (12)$$

and the velocity of the centre of gravity of the doublet multiplied by $m + m''$ is

$$G = \sqrt{m^2c^2 + m''^2c''^2 + 2mm''cc''(\cos\alpha\cos\alpha'' + \sin\alpha\sin\alpha''\cos\beta)} \quad (13)$$

and its component perpendicularly to the plane of central motion is

$$H = \frac{cc'' \sin \alpha \sin \alpha'' \sin \beta}{\sqrt{c^2 \sin^2 \alpha + c''^2 \sin^2 \alpha'' - 2cc'' \sin \alpha \sin \alpha'' \cos \beta}}. \quad (14)$$

The number of doublets in unit of volume for which K, L, G, H lie between the limits

K and K$+d$K, L and L$+d$L, G and G$+d$G, H and H$+d$H,

may be written

$$\Phi(\mathrm{K}, \mathrm{L}, \mathrm{G}, \mathrm{H})\, d\mathrm{K}\, d\mathrm{L}\, d\mathrm{G}\, d\mathrm{H}.$$

The number of these doublets for which ρ lies between ρ and $\rho + d\rho$ is

$$\Phi . d\mathrm{K}\, d\mathrm{L}\, d\mathrm{G}\, d\mathrm{H} . \frac{d\rho}{\sigma} \div \int_{\rho_1}^{\rho_0} \frac{d\rho}{\sigma} = \Psi\, d\mathrm{K}\, d\mathrm{L}\, d\mathrm{G} . d\mathrm{H} \frac{d\rho}{\sigma},$$

in which $\sigma = \frac{d\rho}{dt}$, and $\int_{\rho_1}^{\rho} \frac{d\rho}{\sigma}$ is the time which elapses from a peri-centre to an apo-centre; this latter is, therefore, a given function of K, L, G, H; and $\Psi = \Phi \Big/ \int_{\rho_1}^{\rho_0} \frac{d\rho}{\sigma}$ is likewise a function of these four variables. Let us limit our attention to those doublets for which (1) the last apsidal line of the central orbit makes an angle lying between ϵ and $\epsilon + d\epsilon$ with a straight line drawn in the plane of the orbit parallel to a fixed plane; (2) two planes, one normal to the central orbit and including the direction of motion of the centre of gravity, and the other parallel to a fixed straight line Γ, make angles between ω and $\omega + d\omega$ with each other; and (3) the direction of motion of the centre of gravity lies within a cone of given direction of axis and of infinitely small angle $d\lambda$. We have then to multiply by $d\epsilon\, d\omega\, d\lambda / 16\pi^3$, and the number of doublets in unit volume which fulfil these conditions is

$$\Psi . \frac{1}{16\pi^3 \sigma} d\mathrm{K}\, d\mathrm{L}\, d\mathrm{G}\, d\mathrm{H}\, d\rho\, d\epsilon\, d\omega\, d\lambda. \quad . \quad . \quad (15)$$

If we denote by g and $g + dg$, h and $h + dh$, k and $k + dk$, the limits between which the velocity-components of the centre of gravity of the doublets must lie (the coordinate axes being rectangular and fixed), then

$$\mathrm{G}^2 d\mathrm{G}\, d\lambda = dg\, dh\, dk.$$

Now keep g, h, and k constant, and place at the centre of the shell a system of rectangular coordinates whose z-axis is in the direction of G; denote the coordinates and velocity-components of the nucleus relatively to this system by x_1, y_1, z_1, u_1, v_1, w_1, respectively, and transform these six variables in K, L, H, ρ, ϵ, ω. We then introduce a second system of coordinates, referred to which the coordinates and velocities of the shell are x_2, y_2, z_2, u_2, v_2, w_2, respectively. The z-axis of this second system is to be taken normal to the plane of the central motion, and its x-axis in the section of the plane of

central motion and the old xy-plane. We have then

$$H = G \sin\theta,$$

$90 - \theta$ being the angle between the two axes of z; therefore, since G is constant,

$$dH = G \cos\theta \, d\theta.$$

Finally, let us denote by ω the angle between the two x-axes, seeing that it only differs from the angle previously so designated by a quantity which we are at present regarding as constant. In this case

$$z_2 = x_1 \cos\theta \sin\omega + y_1 \cos\theta \cos\omega + z_1 \sin\theta,$$

$$w_2 = u_1 \cos\theta \sin\omega + v_1 \cos\theta \cos\omega + w_1 \sin\theta,$$

and these two expressions must both vanish, inasmuch as the xy plane is that of the central motion. By means of these two equations we can introduce θ and ω in place of z_1 and w_1, when x_1 y_1 u_1 and v_1 are constants, and we thus obtain

$$dz_1 \, dw_1 = (y_1 u_1 - x_1 v_1) \frac{\cos\theta}{\sin^3\theta} d\theta \, d\omega.$$

Further

$$x_2 = x_1 \cos\omega - y_1 \sin\omega,$$

$$y_2 \sin\theta = x_1 \sin\omega + y_1 \cos\omega,$$

with similar equations for u_2, v_2, u, v. From these it follows that

$$y_1 u_1 - x_1 v_1 = \sin\theta (y_2 u_2 - x_2 v_2) = K \sin\theta,$$

and, if θ and ω are contants,

$$dx_2 \, dy_2 \sin\theta = dx_1 \, dy_1; \quad du_2 \, dv_2 \sin\theta = du_1 \, dv_1,$$

from which

$$dx_1 dy_1 dz_1 \, du_1 \, dv_1 \, dw_1 = K \cos\theta \, dx_2 dy_2 \, du_2 \, dv_2 \, d\theta \, d\omega.$$

Now let us denote, as before, by σ and τ the component velocities of the relative motion of shell and nucleus in the direction of ρ and normal to this direction, respectively; then for constant values of x_2 and y_2,

$$d\sigma \, d\tau = du_2 \, dv_2$$

$$K = \rho\tau, \quad L = L_g + \frac{mm''}{2(m+m'')} (\sigma^2 + \tau^2) + \phi(\rho)$$

$$dK dL = \frac{mm''}{m+m''} \sigma\rho \, d\sigma \, d\tau,$$

where L_g is the energy of motion of the centre of gravity, and

is now constant. Finally, let the angle between ρ and the last apsidal line be ψ, then

$$x_2 = \rho \cos(\epsilon + \psi), \quad y_2 = \rho \sin(\epsilon + \psi),$$

in which ψ is a function of ρ, K, and L; both the latter are now constant, and therefore

$$\rho\, d\rho\, d\epsilon = dx_2\, dy_2.$$

Collecting all these equations we find that

$$dx_1 dy_1 dz_1 du_1 dv_1 dw_1 = \frac{m+m''}{mm''} \frac{\mathrm{K}}{\sigma} d\mathrm{K}\, d\mathrm{L}\, d\mathrm{H}\, d\rho\, d\omega\, d\epsilon;$$

and it will immediately be seen that, if coordinates and velocities without suffix or affix refer to any random set of fixed coordinate axes, we must have likewise

$$dx\, dy\, dz\, du\, dv\, dw = \frac{m+m''}{mm''} \frac{\mathrm{K}}{\sigma} d\mathrm{K}\, d\mathrm{L}\, d\mathrm{H}\, d\rho\, d\omega\, d\epsilon.$$

Introducing this in equation (15) and remembering that for constant values of u, v, and w,

$$dg\, dh\, dk = \frac{m''^3}{(m+m'')^3} du''\, dv''\, dw'',$$

we find

$$\frac{1}{16\pi^3} \frac{mm''^4}{(m+m'')^4} \frac{\Psi}{\mathrm{K}\mathrm{G}_2} dx\, dy\, dz\, du\, dv\, dw\, du''\, dv''\, dw''$$

for the number of doublets in unit of volume for which the variables $x \ldots w''$ lie between x and $x + dx \ldots w''$ and $w'' + dw.''$ But we have previously found for this number the expression

$$\mathrm{F} \,.\, dx\, dy\, dz\, du\, dv\, dw\, du''\, dv''\, dw'',$$

and we then saw that F must be of the form $\mathrm{A}\epsilon^{-\kappa mc^2}$, in which A is a function of c'', ρ, and α'' only. It follows then, if we write

$$\mathrm{F} = \mathrm{B}\epsilon^{-\kappa(mc^2 + m''c''^2 + 2\phi(\rho))},$$

that B must be on the one hand a function of c'', ρ, and α'' only, and on the other hand a function of K, L, G, and H only. B must therefore be a function of these latter variables which is quite independent of c, α, and β, and only a function of c'' ρ, and α''.

If we put $\mathrm{B} = f(\mathrm{K}, \mathrm{L}, \mathrm{G}, \mathrm{H})$, then this function must be independent of c, α, and β, for all values of c'' and α''. Substitute for the variables K, L, G, H their values from 11, 12, 13, and 14, and make $c'' = 0$ at first. Then

$$\mathrm{K} = \rho c \sin\alpha, \quad \mathrm{L} = \tfrac{1}{2}mc^2 + \phi(\rho), \quad \mathrm{G} = mc, \quad \mathrm{H} = 0.$$

$$\mathrm{B} = f\left(\rho c \sin\alpha, \frac{mc^2}{2} + \phi(\rho), mc, 0\right).$$

As this expression is independent of c and α the function f does not contain the quantity K, and it only involves L and G in the form $2m\mathrm{L}-\mathrm{G}^2$. We can best express this by writing the function with variable $2m\mathrm{L}-\mathrm{G}^2$, instead of L, G, when it becomes $\mathrm{B}=f(2m\mathrm{L}-\mathrm{G}^2,\mathrm{H})$. If we introduce again into this expression the general values given in equations 11 to 14, we see that the two variables in the function are quite independent of each other if c, α, β are to have all possible values. And since B is constant for all values of c, α, and β, it is so for all values of $2m\mathrm{L}-\mathrm{G}^2$ and H, and is therefore absolutely constant. The distribution of *vis viva* is therefore obtained.

XXII. *The Fusion Constants of Igneous Rock.*—Part II. *The Contraction of Molten Igneous Rock* on Passing from Liquid to Solid.* *By* Carl Barus †.

[Plate V.]

Introductory.

1. *Material and Method.*—The following volume-measurements were made for Mr. Clarence King, on a typical sample of diabase which he furnished.

The method of testing the volume-behaviour by allowing the rock to expand in a vertical tube provided with an index was suggested to Mr. King by Lord Kelvin. I therefore preferred it to a method of my own ‡, in which the behaviour in question is to be determined by high-temperature air-volumetry, with the rock enclosed in a *glazed* platinum bulb-and-stem arrangement. In place of the index or float I employed an electric micrometer, believing a probe of this kind to be more trustworthy (§ 13). I may state here, that the fact that the contraction of the magma in passing from liquid to solid can actually be measured by the simple burette method was to me a great surprise. After many trials I found, however, that by allowing the furnace to cool so *slowly* that the platinum vessel remained rigid relatively to the charge, the contraction of the latter could be followed even into the solid state. As a consequence of slow cooling, moreover, the magma was probably undercooled, and I thus obtained the whole volume-difference liquid-solid at a given temperature. The data are

* *Cf.* note in American Journal, xlii. p. 498 (1891).

† Communicated by the Author.

‡ *Cf.* Phil. Mag. July 1892, where this method is tentatively employed to measure the expansion of white-hot porcelain.

sufficient to compute the corresponding contraction at other temperatures.

2. *Literature.*—The question has elicited voluminous discussion; but literary comments are superfluous here, since Prof. F. Niess*, of Hohenheim, not long ago made a careful survey of all that has been done on the subject. The reader desiring specific information is referred to this interesting pamphlet. "Es ist ein durch Contraste buntes Bild," says Prof. Niess (*loc. cit.* p. 36), "welches in der vorstehenden Citatenlese dem Leser zu entrollen war, und aus dem Wirrwarr entgegengesetzter Ansichten heben sich nur zwei Körper: Wismuth und Eisen, heraus, über welche man wohl mit absoluter Sicherheit die Acten als geschlossen bezeichnen kann, und zwar in dem Sinne, dass für sie die Ausdehnung im Momente der Verfestigung als zweifellos bewiesen gelten kann. Die übrigen Metalle stehen noch im Streit, und für sie gilt dasselbe was wir für die künstlichen Silicate zu fordern hatten . . . . ." Now iron, in virtue of the occurrence of recalescence (Gore, Barrett), is scarcely a fair substance to operate upon; and it heightens the confusion to find that Prof. Niess, after weighing all the evidence in hand, is obliged to conclude that rocks expand on solidifying.

The present experiments show beyond question, I think, that at least for diabase this is not true. I find that this rock not only contracts between 3·5 and 4 per cent. on solidifying, but that such solidification is sharply broken and only apparently continuous with temperature, and that the fusion-behaviour throughout is quite normal in character. Hence, with certain precautions which I shall adduce in the course of this paper (§ 21), the volume thermodynamic relations which I derived by acting on organic bodies may be applied to rock magmas.

3. *Effect of Fusion. Density.*—The rock after fusion is changed to a compact black obsidian, and quite loses its characteristic structure. It was therefore important to examine the volume-relations of this change, preliminarily. This is done in Table I., where the densities obtained with lumps of the rock (mass M) at the temperature t are given, Δ being the density before, Δ' after fusion.

* "Ueber das Verhalten der Silicate etc.," *Programm zur* 70. *Jahresfeier d. k. Würtemb. landw. Academie*, Stuttgart, E. Koch, 1889. *Cf.* Niess u. Winkelmann, Wied. *Ann.* xiii. p. 43 (1881); xviii. p. 364 (1883).

TABLE I.—Density of Diabase before and after Fusion.

Before Fusion.				After Fusion.				
Sample No.	M.	t.	Δ.	Sample No.	M.	t.	Δ'.	$\frac{\Delta-\Delta'}{\Delta}$.
	g	°C.			*g*	°C.		
I.	22·8950	25	3·0161	*I.	69·9330	21	2·7018	·104
II.	45·3654	21	3·0181	†II.	33·7659	19	2·7447	·090
III.	54·7208	21	3·0136	†III.	29·9777	19	2·7045	·103
IV.	69·4940	21	3·0235					

The rock was fused both in clay and in platinum crucibles. In the latter case the density of the known mass of metal had been previously determined, and the glass was not removed from the crucible. In the other case the clay was broken away from the solid lump within, and its density then measured directly. A few small bubbles were visible on the fresh fracture of the glass, due, I presume, to the ejection of dissolved gases on solidification. At some other time I will make vacuum-measurements of the density of powders both of the rock and the glass, but I do not believe the data of Table I. will be seriously changed by such a test.

From Table I. it appears that the mean density of the original rock is 3·0178; that of the glass after fusion is only 2·717, indicating a volume *increment* of 10 per cent. as the effect of fusion. This remarkable behaviour is not isolated. Niess (*l. c.* p. 47), quoting from Zirkel's *Lehrbuch*, adduces even more remarkable volume-increments of the same nature‡; viz., in garnet 22 per cent., in vesuvianite 14 per cent., in orthoclase 12 per cent., in augite 13 per cent., &c.: but I doubt whether the great importance of these facts has been sufficiently emphasized. Suffice it to indicate here that it makes an enormous difference into what product the magma is to be conceived as being solidified; and that throughout this paper the molten rock solidifies into a homogeneous obsidian. I am only determining, therefore, those volume-

* Fused in a clay crucible. Glass detached when cold.

† Fused in a platinum crucible. Glass not detached.

‡ *Cf.* Thoulet, *Ztschr. f. Kryst. u. Mineralogie*, v. p. 407 (1881); *Bull. Soc. Min. de France*, iii. p. 34 (1880).

changes which lie at the margin, as it were, of the more profound and chemically significant volume-changes (polymeric passage from homogeneity to organized rock-structure), even though the latter may be conceived as producible by pressure alone, under conditions of nearly constant (high) temperature. I may add, in passing, that the magnitude of the chemical changes of volume makes it advisable to carry the work on the effect of pressure on the chemical equilibrium of solids and of liquids, and on the solution behaviour solid-liquid, into greater detail than I have thus far attempted*.

Apparatus.

4. *Temperature Measurement.*—In work of the present kind an apparatus for the accurate measurement of high temperatures is the fundamental consideration. I may, however, dismiss this subject here, since I discussed it in the introductory paper†. The temperature-measurements of this paper were made with a thermocouple of platinum and platinum with 20 per cent. of iridium, which had been frequently compared with my re-entrant porcelain air-thermometer throughout an interval of 1100° C., and tested for freedom from anomalies beyond this interval. Inasmuch as the electric method consists in expressing thermoelectromotive force by aid of a zero method, in terms of a given Latimer-Clark standard cell, the temperature-apparatus is of the same order of constancy as to time as the standard cell.

To find in how far my earlier data were trustworthy after the lapse of upwards four years, I made fresh check measurements of the boiling-points of mercury and of zinc. The latter only need be instanced here. My original mean datum of the boiling-point of zinc, expressed as electromotive force for the couples under consideration, was (1887) $e_{20}=11{,}074$ microvolts, the cold junction being at 20° C. The new experiments (1891) gave me data as follows:—

Thermocouple	No. 35,	e_{20} =	11,168	(microvolts),
„	No. 36,	„	11,127	„
„	No. 39,	„	11,116	„
„	No. 40,	„	11,136	„
	Mean . . .		11,137	„

* American Journal, xxxvii. p. 339 (1889); ibid. xxxviii. p. 408 (1889); ibid. xl. p. 219 (1890); ibid. xli. p. 110 (1891); ibid. xlii. p. 46 *et seq.* (1891). Also Phil. Mag. [5] xxxi. p. 9 (1891).

† See this Magazine, July 1892, p. 1.

agreeing very closely with subsequent specially careful measurements, viz.:—

Thermocouple No. 36, e_{20} = 11,131 (microvolts),
„ No. 39, „ 11,134 „

The difference of values, new and old, is 60 microvolts, only about ½ per cent. as regards electromotive force, and corresponding to about 4° at 1000°. In view of the excessive use and abuse to which the couples had been put in the lapse of time this result is gratifying.

Endeavouring to ascertain where this discrepancy was to be sought, I also made new comparisons between the Clark cell and a normal Daniell of my own (Bull. 54, U. S. Geolog. Survey, p. 100), in which the cells are separate, and only joined during the time of use. Supposing the electromotive force of the former to have been e=1·435 throughout, the following succession of values obtained for the standard Daniell:—

March	1886,	20° C.,	e=1·138,
August	1887,	28° C.,	1·139,
September	1891,	27° C.,	1·147.

If, therefore, instead of regarding the Clark cell as constant I had attributed* this virtue to the standard Daniell, the small thermoelectric discrepancy equivalent to 4° at 1000° would be altogether wiped out. Now I made the Clark cells in question as far back as 1883, when less was known about details of construction than is now available. I conclude, therefore, that the discrepancy is very probably in the standard cells, and that the thermocouples have remained absolutely constant, a result which is borne out by my boiling-points of cadmium.

Apart from this, the new standardization with boiling zinc fixes the scale relatively to the accepted value for this datum.

5. *General disposition of Apparatus.*—This is given in Plate V. on a scale of 1 : 4, where figs. 1 and 3 are sectional elevations showing the parts chiefly with reference to their vertical height, and fig. 2 is a sectional plan, in which the parts are given with reference to the horizontal.

The molten rock, Z Z, contained in a long cylindrical platinum tube, largely surrounded by a tube of fire-clay, F F, is fixed vertically in a tall cylindrical furnace, D D, L L. The heat is furnished by six burners, B, B, . . . , fed by gas and an

* Our laboratory affords insufficient facilities for the direct measurement of electromotive force.

air-blast, laden, if need be, with oxygen. These burners are placed at equal intervals along the vertical, three on one side and three on the other (see fig. 2), and set like a force-couple, so as to surround the platinum tube with a whirlwind of flame. Suitable holes are cut in the walls of the furnace for the symmetrical insertion of the insulated thermocouples, T, and also at S for fixing the sight-tubes, A, near the top and the bottom of the furnace. Parts of the envelope of the platinum tube are cut away, so that the upper and lower ends of the (red hot) platinum tube can be seen in the telescope of an external (screened) cathetometer. Thus the expansion of the platinum tube is measured directly. A vertical micrometer, K *k d* (figs. 3 and 4), insulated so as to admit of electrical indications of contact, furnishes a means of tracing the apparent expansion of the rock Z Z, within the fusion-tube.

In principle, the excessively slow cooling of the furnace is to be so conducted that the magma may always remain much less viscous than the practically rigid platinum envelope (§§ 1, 18).

The furnace stands on a massive iron base perforated by eight holes, into which vertical iron uprights are screwed, symmetrically surrounding the furnace and at a distance of 4 or 5 centim. from its circumference. Only one of these is indicated at Q Q (fig. 3), the rest with other subsidiary parts being omitted to avoid confusing the figure. Two of these uprights hold the vertical micrometer, two hold the burners in place, and two subserve as buffers for the clay arms, H, H,... by which the fusion-tube is adjusted vertically. The sight-tubes are suitably clamped to the seventh and the insulators of the thermocouples to the eighth. All these uprights are hollow, and a swift current of *water continually circulates* through them, issuing still cold to the touch. The same current also flows through the bent screen, X X, of the vertical micrometer, and through the vertical flat screen of the cathetometer.

6. *The Furnace.*—The burners, B, are each fed with the same amount of gas and air by properly branching the large supply-tubes. A graduated stopcock is at hand for regulating the supply of gas to a nicety. Hence the furnace is fed with a mixture of gas and air, and temperatures between 400° and 1500° are obtained by simply making the influx poorer or richer in combustible gas. Oxygen has not thus far been necessary*.

* Burners suitable for the above purpose are shown in my little book on high temperatures (Leipzig, Barth, 1892).

The products of combustion are carried off by the two oblique tubes, E, E, in the lid L L (fig. 4). Note that the water-screen bends around the vertical micrometer in such a way that flames issuing from E do no injury, and a perforated free plate, *m m*, closes the vertical hole in the lid L L.

Two large size Fletcher-bellows, set like a duplex-pump and actuated by a gas-engine, furnished the air-blast.

In order to insure greater constancy of temperature, and at the same time increase the high temperature efficiency of the furnace, it is essential to jacket both the latter and the lid heavily (1–2 centim.) with asbestos.

7. *Fusion-tube.*—The platinum tube holding the molten rock Z Z is 25 centim. long and about 1·5 centim. in diameter, drawn as accurately cylindrical as possible and provided with a flat bottom. To protect this tube from gases, to keep it from bulging in consequence of the fluid-rock pressure within, and to insure greater constancy and slower changes of temperature, the platinum tube is surrounded by the fire-clay tube F F (figs. 1 and 6) fitting loosely. Care must be taken to allow for shrinkage of the clay, which in a fresh tube, after some hours' exposure to 1500°, exceeds 3 per cent. or more, and is permanent. After this the tube expands normally. It rarely warps, and may therefore be fixed by fire-clay arms, H (figs. 1, 2, and 7), suitably clamped on the outside of the furnace. Near the bottom a perforated ring, C C (figs. 1 and 5), embraces both the tube F F and a projection, G, in the furnace.

8. *Thermocouples.*—In addition to figs. 1 and 2, figs. 6 and 8 give a full account of the adjustment. The tube F F is laterally perforated with three pairs of fine holes, *t*, corresponding to the two canals of the insulator*, T T. The wires of the thermocouple are then threaded through *t* and the insulator canals, in such a way that the respective junctions lie in small cavities at *t*, immediately in contact with the outside of the platinum tube. Holes are left in F F and the furnace for this operation.

The cold junctions of the thermocouples terminate in three pairs of mercury-troughs, insulated by hard rubber, and submerged in a bath of petroleum. With these troughs the terminals of the zero method are successively connected, and the temperatures of the top, the middle, and the bottom of the fusion-tube measured by § 4.

* The method of making these is given in Bull. No. 54, U. S. Geolog. Survey, p. 95.

9. *Sight-tubes.*—Grunow's excellent cathetometer is placed on a pier, so that the prism of the instrument is only about 50 centim. off from the fusion-tube. A tall, hollow screen, 30 centim. broad, 70 centim. long, and 1 centim. thick, fed with cold water, and movable on a slide, is interposed between furnace and cathetometer. Slots, cut through the screen and closed by plate glass, correspond to the two positions of the telescope ; and the lines of sight pass through S, S, near the top and the bottom of the furnace (see figs. 1 and 2). Thus the ends of the fusion-tube, one of which projects above the clay tube F F, and the other is seen through the perforation O in C C (figs. 1 and 5), appear as sharp lines in the telescope, against the red-hot background of clay.

It is necessary, however, to prevent the escape of flame and gas at S, and hence these holes are provided with porcelain tubes A (only one shown in the figure) about 15 centim. long, the outer end of which is ground off square and closed with a piece of plate glass *b*, by aid of a clamping device *aa*.

10. *Vertical Micrometer.* — Figures 3 and 4 give a full account of this instrument (also made by W. Grunow), both of which are sectional elevations at right angles to each other. The millimetre-screw plays easily through the massive block of brass, P P, and the fixed lock-nut *g g*. P P is bolted down to the rigid bridge of brass, N N, by means of screws, R R, and the counterplate U U. The ends of N N are provided with sleeves, *p p*, and a clamp-screw, M, whereby the whole micrometer may be moved up or down or fixed in any position along the uprights, Q Q. To secure insulation of the screw K *k*, R, R are surrounded by jackets *n*, *n* of hard rubber, and plates, *i*, *j*, *q* of this material are suitably interposed between P P, N N, U U, and other parts.

Sufficiently wide slots are cut in the bridge, N N (see figures), whereby the plate may be shifted in any direction, and then clamped in position.

In view of the heat which rises from the furnace, an N-shaped screen, X X, through which water rapidly circulates (entering and leaving at diagonally opposite points, V and Y, at the top), nearly envelopes the micrometer. The micrometer-screw passes through a narrow tube in the bottom of XX ; hence the screen must also be adjustable, and a way is shown in the figure. Thus the micrometer and its water-screen slide as a single piece, along the upright Q Q. Q and Y are joined by a sufficient length of rubber hose, a connexion merely indicated in the figure.

Finally K *k* is prolonged by a straight cylindrical tube of platinum *d d*, which may be fixed to the steel rod *k* by the clamp *e* in any position along the vertical. The tube fits the rod *k* singly, and a special steel rod is provided by which the tube may be straightened, should it become warped.

The lower end of *d* is clearly visible in the telescope of the cathetometer, through the sight-tube A. On being screwed down, *d* enters the fusion-tube axially, supposing both tubes (*d* and Z Z) to have been properly fixed in position. In how far such adjustment has been made, can be seen by temporarily removing one of the efflux tubes, E (fig. 4), when the parts concerned are visible to the eye.

11. *Telephonic Registration.*—Since it is necessary to find the depth of the meniscus of the molten rock Z Z below the plane of the top of the fusion-tube, the moment of contact of Z Z and *d* is registered electrically. Above, say, 500° C., rock is a good conductor. Hence, if a current be passed into the screw K *k*, through the clamp-screw *f* (fig. 3), it will issue at the bottom at the clamp-screw *c* (fig. 1), provided *c* be electrically connected (platinum wires) with the bottom of the fusion-tube, Z Z.

A telephone actuated by Kohlrausch's small inductor is more convenient for the present purpose than a galvanometer. Contact is then indicated by a loud roar, and the observer's attention is not further distracted. If the glass Z Z be sticky, the drawing out of a thread corresponds to a more or less gradual cessation of the noise, so that the character of the fusion can be pretty well indicated in this way. Care should be taken to insure a small sparking-distance.

If the expansion of the rock be known, and the tube *d d* be sunk deeply into the mass, it is clear that the present method admits of a measurement of the relation of the electric resistance of the glass and temperature. I mention this, believing that not only will a suitable method of temperature measurement be thus available, but that the volume diagrams, constructed below, may also be derived solely from measurements of electrolytic resistance *.

Method of Measurement.

12. *Consecutive Adjustments.*—Thus far I have only studied rock-contraction. For this purpose, the graduated faucet,

* *Cf.* Am. Journ. Sci. xlii. pp. 134–35 (1891), where I have already speculated on the character of electrolytic resistance referred to temperature.

§§ 5, 6, is turned on in full, and the furnace fired as far as 1400° or 1500°, when the measurements may be commenced. The length of the fusion-tube is first accurately measured by cathetometer observations at the bottom and the top. The telescope is then left adjusted for the top, and the vertical micrometer (centrally fixed) screwed down until the image of its lowest point is in contact with the cross hairs. After this the micrometer is further screwed down, until the telephone indicates contact between the platinum micrometer-tube and the meniscus of molten rock. The difference of readings gives the depth of the latter below the top plane of the fusion-tube. I usually repeated these measurements three times.

Hereupon the temperature measurements were made by connecting the terminals of the zero method with the lower, the middle, and the upper thermocouple.

Finally, the cathetometer and micrometer measurements were again repeated in full. Uniform heating presupposed, it was permissible to regard the two sets of length measurements as coincident with the intermediate temperature measurement.

This done, I frequently waited 15 minutes or more, to make another complete measurement, under better conditions of constant temperature.

The graduated stopcock was then partially closed by a proper fractional amount, and after waiting a sufficiently long time, the same series of measuring operations was gone over again. Thus I continued until the glass became sticky and solidification imminent, when longer waiting and more finely graded changes of temperature were essential. Fortunately the observer can infer the state of fusion very well, by noting the time necessary for the glass threads drawn out by the micrometer to break, § 11. Finally, the enamel on the end of the micrometer-tube becomes solid and ceases to change its form, simultaneously with which the marked contraction of the molten mass in the fusion-tube begins.

Having waited long enough for the lowest position of the meniscus, temperature may be varied in larger steps again.

When the furnace is dark, measurement is no longer possible. I then allowed the whole arrangement to cool over night, and next morning determined both the depth of the solid meniscus and the length of the cold tube. The former was computed from bulk measurements (with water) as well as measured micrometrically. These are the normal or fiducial data to which all the other volumes were referred.

13. *Computation.*—Let the linear expansion of the platinum fusion-tube be given by $l=l_0(1+f(t))$, where l and l_0 are the lengths at t degrees and at zero respectively. Let λ and λ_0 be the depths of the meniscus below the plane of the top of the fusion-tube, and v and v_0 the volumes of the enclosed molten magma at t and zero respectively. Then, if $(1+f(t))^3$ is nearly enough $1+3f(t)$; if the expansion constants of the fusion-tube and of the micrometer-tube be the same, and if in consideration of the small motion of the latter and the high temperature in the furnace, the air temperature outside of it be nearly enough zero, since

$$v_t/v_0=(l_0-\lambda)(1+f(t))^3/(l_0-\lambda_0),$$

$$(v_t-v_0)/v_0=3f(t)+(\lambda_0-\lambda)(1+3f(t))/(l_0-\lambda_0). \quad . \quad (1)$$

Here $3\ f(t)$ is directly given at each observation, or may be computed by some smoothing process from the data as a whole.

The equation, therefore, gives the actual expansion of the rock, in terms of unit of volume of solid rock at zero Centigrade. If this be multiplied by the initial specific volume, the absolute expansion is obtained. An inspection of (1) shows that in the factor $\lambda_0-\lambda$, the micrometer value of the length λ is to be inserted in both cases, supposing the contour of the meniscus to remain similar to itself; whereas in $l_0-\lambda_0$ the value of λ_0 determined from bulk measurements of the space at the top of the cold tube is suitable, since the tube is flat-bottomed.

I may add in passing that if δH be the rise of a flat-bottomed cylindrical float of platinum, submerged to a depth h in a column of magma of height A, then nearly

$$(v_t-v_0)/v_0=3f(t)+\delta\mathrm{H}/(\mathrm{A}-h). \quad . \quad . \quad . \quad . \quad (2)$$

Since, therefore, the float shortens the efficient length of the fusion-tube and there is difficulty in determining A in this case, the above micrometric method is preferable quite aside from flotation errors due to viscosity and capillarity, to the easy welding of white hot platinum surfaces, to the tendency of gas bubbles to accumulate on the surface of the float, to the cessation of true flotation during the change from liquid to solid, &c.

14. *Errors.*—The change of temperature from top to bottom of the fusion-tube is measured. The change of temperature from circumference to axis of the fusion-tube is *nil*

in proportion as the furnace cools slowly. The latter condition is met at least so long as glass is liquid, and data for the former are fully given below. To avoid strains of dilatation it would be desirable to make the glass solidify from the bottom upward. This, however, my furnace as yet fails to do. Indeed, I have frequently noted lateral holes shaped like an inverted funnel and terminating in the otherwise smooth surface of the meniscus. This may indicate the occurrence of gas bubbles under the free surface or be a strain effect, § 3. The tendency of these nearly unavoidable difficulties is to make the solidification contraction too small; and I have therefore not been disturbed by them.

Only at very high temperatures (above 1500°) did I obtain apparent evidence of the viscosity of platinum relatively to the pressure of the column of 25 centim. of molten rock, whereas the combined system of platinum and clay tube withstood this pressure. There is also a slight deepening of the meniscus from day to day, and a similar decrease of the length of the platinum fusion-tube; but, thus far, I have encountered no serious error due to the high temperature viscosity of the vessel, § 18.

The assumption that the meniscus remains similar to itself in form at all temperatures cannot be quite true. At white heats, however, the glass wets platinum so thoroughly that convex forms of meniscus need never be apprehended. It is futile, however, to endeavour to make allowance for meniscus; but data for the difference between the (cold) bulk and micrometric measurements are given below. Although too much reliance must not be placed on the behaviour of the solid state, yet the values are redeemed from the character of mere estimates by the close coincidence of the expansion of platinum and its solid glass core. Strains imposed on both the metal and the glass do not probably exceed the limits of elasticity of either, §§ 17, 18. When cooling is conducted slowly enough, the experiments show that the platinum tube is not dragged along seriously by the solidifying magma; and the data thus retain a degree of trustworthiness greater than was anticipated, even in the solid state. At the same time dilatational strain is reduced to a minimum, and constancy of temperature throughout efficient parts of the furnace is promoted.

One error much in my way thus far has been the allowance to be made for the expansion of the platinum probe *dd* (fig. 3). It is not merely the amount by which the probe is lowered that is subject to expansion, but a considerable length of the

metallic screw K*kdd* passes from a lower to an indeterminable higher temperature. I hope, however, in the future to obtain an estimate for this discrepancy, by measuring a given amount of thrust through the sight-tube with the cathetometer, and comparing this value with the corresponding value to be read off on the vertical micrometer. Hollow screws and water circulation would be exceedingly difficult to attach here.

Results.

15. *Arrangement of the Tables.*—In the following tables l and v_0 denote the length and radius of the (cold) fusion-tube, and λ_0' the bulk value (water measurement) of the mean depth of the meniscus, these measurements being made on the day after the fusion experiments. The temperatures at the bottom, the middle, and the top of the fusion-tube are given under θ_1, θ_2, θ_3, respectively. For each value of mean temperature θ, two data for the apparent expansion of the rock, for the volume-expansion of the fusion-tube, and for the actual volume-expansion, $(v_t - v_0)/v_0 = \delta v/v_0$, of the rock are given, and they were obtained before and after the intermediate temperature measurement, respectively. Reference is thus made to unit of volume of solid rock at zero Centigrade, throughout. The data enclosed in parentheses show that for them, the value applied for the expansion of the fusion-tube is obtained as a mean result of all the measurements made, otherwise the value directly observed was directly applied. The chief constants are summarized at the end of each table.

16. *Contraction of Diabase. Series* I. *and* II.—The results of these series, being of inferior accuracy and serving chiefly to substantiate the remarks of § 14, may be omitted here. They showed a liquid volume-expansion of $50/10^6$ per degree, a solid expansion of $20/10^6$ per degree, and a solidification contraction of about 3 per cent. only, owing to the occurrence of dilatational strain.

17. *Contraction of Diabase. Series* III., *Tables.*—This work was done on October 20, 1891, and the data are given in Table II. Precautions for slow cooling were fully taken, and the solidification point is therefore sharply apparent. The results will be discussed in connexion with the next series.

TABLE II.—Contraction of Diabase. Series III.

$l_0 = 25{\cdot}466$ centim., $\lambda_0 = 1{\cdot}424$ centim., $r_0 = {\cdot}75$ centim.

θ_1. θ_2. θ_3.	Mean θ.	Apparent volume-expansion of Rock.	Volume-expansion of the tube.	$\delta v/v_0$.	Mean. $\delta v/v_0$.	Time.	Remarks.
°C.	°C.	$\times 10^4$.	$\times 10^4$.	$\times 10^4$.		Minutes.	
1360	1386	452	358	810	·0811	0	Liquid.
1396		454	(356)	812	(·0809)		
1403				(808)			
				(810)			
1286	1300	437	340	777	·0778	23	Liquid.
1304		438	(334)	778	(·0772)		
1311				(771)			
				(772)			
1163	1166	406	297	703	·0704	53	Sticky.
1167		409	(300)	706	(·0707)		
1168				(706)			
				(709)			
1097	1093	376	270	646	·0646	86	Very sticky.
1093		333	(281)	603	.....		To be drawn
1089				(657)	(·0657)		out in threads.
				(614)	.....		Eventually solidifying.
1102	1095	14	273	288	·0287	111	Solid.
1095		13	(282)	286	(·0296)		
1088				(296)			
				(295)			
929	896	0	211	211	·0212	157	Solid.
897		2		(213)			
863							
461	468	−4	81	77	·0079	185	Solid.
433		0		81			
510							
	20	0	0	0	·0000	Next day.	Cold.

Rock, mean actual expansion, solid, 0°–1000° . .	·0000250
,, ,, ,, ,, liquid, 1100°–1500° .	·0000470
,, contraction on solidification (1094°) . . .	·0390
Rock, mean apparent expansion, solid, 0° 1000° . .	·0000007
,, ,, ,, ,, liquid, 1100°–1500°	·0000205
Tube, mean volume-expansion below 1000° . . .	·0000240
,, ,, ,, ,, above 1100° . . .	·0000265

18. *Contraction of Diabase. Series* IV. *Tables and Chart.*—The data of the last series of experiments (made on October 21, 1891) are given in Table III. Two complete sets of results correspond to each step of temperature.

TABLE III.—Contraction of Diabase. Series IV.

$l_0 = 25{\cdot}447$ centim., $\lambda_0' = 1{\cdot}220$ centim., $r_0 = 75$ centim.

θ_1. θ_2. θ_3.	Mean. θ.	Apparent volume-expansion of Rock.	Volume-expansion of the tube.	$\delta v/v_0$.	Mean. $\delta v/v_0$.	Time.	Remarks.
°C.	°C.	$\times 10^4$.	$\times 10^4$.	$\times 10^4$.		Minutes.	
1374	1388	403	357	760	·0760	5	Liquid.
1394		404	(356)	761	(·0760)		
1395				(759)			
				(760)			
1415	1421	407	362	768	·0770	20	Liquid.
1431		409	(364)	771	(·0771)		
1417				(771)			
				(773)			
1318	1319	394	341	734	(·0731)	50	Liquid.
1324		387	(339)	727	(·0730)		
1315				(733)			
				(726)			
1304	1305	383	350	733	·0736	65	Liquid.
1308		390	(335)	740	(·0721)		
1304				(718)			
				(725)			
1204	1190	357	316	673	·0672	90	Sticky.
1189		355	(305)	671	(·0661)		
1176				(662)			
				(660)			
1177	1163	355	299	655	·0652	105	Very sticky.
1158		349	(299)	649	(·0652)		To be drawn
1153				(655)			out in threads.
				(649)			
1138	1112	339	286	625	·0628	128	Top en-
1109		344	(286)	630	(·0628)		crusted.
1090				(625)			
				(630)			
1117	1092	200	275	475	·0475	151	Solidifying.
1088		155	(280)	430	(·0480)		
1072		91		366			
1109	1092	33	282	315	·0287	175	Solidifying,
1081		5	(280)	287	(·0285)		
1086							
946	914	13	213	226	·0223	198	Solid.
903		6		220			
893							
900	855	3	199	202	·0202	210	Solid.
827		3		202			
837							
	20	0	0	0	·0000	Next day.	Cold.

Rock, mean actual expansion, solid, 0°–1000° . . . ·0000250
" " " " liquid, 1100°–1500° . ·0000468
" contraction on solidification, at 1092° . . . ·0340

Rock, mean apparent expansion, 0°–1000° . . . . ·0000005
" " " " 1100°–1500° . . ·0000218

Tube, mean volume-expansion below 1000° . . . ·0000235
" " " " above 1100° . . . ·0000260

These data are given in the chart (fig. 10), temperatures in degrees C., as abscissæ, volume-changes as ordinates. A chart of the same character may also be constructed from Table II., but this is superfluous. In figure 10 the actual expansion of the rock is shown by the heavy line *dcbef*, and the numbers attached to the points of observation indicate the times at which they were made. The apparent expansion of the rock is shown by the light line *lkgh*, where the ordinates of the solid contour are nearly zero. Finally the expansion of the fusion-tube is represented by the dotted line *dcai*. The amount of break at *a*, which is even smaller in Series III., indicates the amount of drag or a shortening of the length of the platinum tube by the solidifying rock within, and furnishes an estimate for the trustworthiness of the solid results. It is interesting to note that in both Series III. and IV. the first length measurements of the tube are smaller than the second at the same temperature, showing that the tube has to some extent recuperated from the strain, or that the amount of end thrust has diminished. It is similarly possible to note the sag as expressed by the cold lengths (25·49 centim. in Series II., 25·47 centim. in Series III., and 25·45 centim. in Series IV.) of the platinum fusion-tube. Finally, the depth of the liquid meniscus at the outset of Series III. and IV., and at about the same temperature, was $\lambda = \cdot 50$ centim. and $\lambda = \cdot 62$ centim., showing enlargement of the bulk of the tube. These changes, which are in part allowed for, show that viscosity introduces no serious discrepancy. Regarding the differences of λ_0 and λ_0' the remarks made in § 14 apply.

An inspection of the curve *dbef* as a whole indicates the occurrence of sharply marked solidification at 1093°. This is sufficient evidence to prove that rock-fusion (diabase) is thoroughly normal in type. A method is thus given in which the solidifying-point is determined free from non-intrinsic tests.

Finally, the contraction on solidification, 3·9 per cent. in Series III., and 3·4 per cent. in Series IV., is established, for diabase at least, beyond question. It is to be noted, moreover, that the smaller value (IV.) corresponds to a larger drag during solidification on the platinum tube (*cf.* Tables II. and III.). Hence the value 3·9 per cent. is the more probable. In general, temperatures (θ_1, θ_2, θ_3) are nearly alike so long as the glass is liquid. This ceases to be the case after solidification; and since the top of the fusion-tube is apt to be colder than the bottom, some of the solid contraction expresses itself in dilatational strain, § 14.

19. *Flotation.*—Naturally I made a few tests on the flotation of solid rock on the molten magma. *Cf.* § 3. To my surprise such flotation usually occurs, notwithstanding the fact that the original cold rock may be 8 per cent. + 10 per cent. more dense than the molten magma. The cause, however, is crudely mechanical, since the rock, in virtue of its weight and temperature, hollows out a cavity and chills its surface simultaneously, forming a little boat in which it floats on the very viscous liquid below. This is indicated in fig. 9, where *a* is the body of rock, AA the molten magma, and *bb* the solidified skin. I also attempted to make Niess and Winkelmann's "Fundamentalversuch" (Niess, *l. c.* p. 16), by submerging the rock; but here, both on account of the intense white glare of the furnace and the tendency to chill at the surface, I did not reach a definite point of view.

Inferences.

20. *Hysteresis.*—In the above experiments I have only studied the solidifying magma. It does not appear, therefore, whether solidification and fusion take place at identical temperatures, or whether they will comprehend a volume-lag.

In other work, in which the rock of the fusion-tube was alternately fused and solidified, the loci are cyclic in marked degree, covering considerably more than 50°. It so difficult, however, to discriminate between true hysteresis and the accompanying discrepancy due to insufficiently rapid heat conduction as compared with the insufficiently slow change of temperature, that experiments made with a tube which is not at quite the same temperature throughout its length are not unassailable. Having failed to perfect the experiments, I omit the data altogether.

21. *Melting-point and Pressure.*—Since the fusion of rocks like diabase is thoroughly normal, it follows that melting-point must increase with pressure. It is well to examine tentatively into the nature of this relation, and for this purpose I have constructed certain unpublished results of mine for thymol, in the same scale as used for the rock, in fig. 11. The curve $m'n'o'p'$ shows the contraction of thymol at its melting-point (somewhat below 50°), where the substance is liquid along $o'p'$ and solid along $m'n'$. The curve $m\,n\,o\,p$ similarly applies at 0° C. It is seen, therefore, that here solidification contraction and thermal expansion (solid or liquid) decrease together. This is also true on passing from thymol to the rock. Could liquid thymol be cooled down as far as −25°, it would then show the same solidification contraction as the silicate.

Analogously the latter must show decidedly smaller compressibility than the organic body, and hence it follows that whereas the lower critical pressure (solid-liquid) of naphthalene, for instance, lies in the region of some 10,000 atmospheres in my experiments, the corresponding (critical) pressure of the rock magma will be indefinitely higher.

From this, however, it is by no means to be inferred that the relation of melting-point to pressure ($d\theta/dp$) will be different in the silicate and in the carbon compound. In the latter case data for normal fusion are available for wax, paraffin, spermaceti, and naphthalene. These lie within a margin of ·020 to ·036. Taken into consideration with the difficulty of obtaining these data, the preliminary character of the experiments, the lack of crystalline definiteness in many of the compounds, and the fact that even for the same substance* the coefficient may vary as much as ·027 to ·035, the said margin may reasonably be regarded as narrow. It appears to me probable, therefore, since fusion in the organic bodies and the silicate is alike in type, that the same factor $d\theta/dp$ will correspond to both cases.

Direct evidence in favour of this view will be adduced in my next paper.

XXIII. *On a certain Asymmetry in* Prof. Rowland's *Concave Gratings. By* Dr. J. R. Rydberg, *Docent of Physics at the University of Lund, Sweden* †.

I. In order more especially to obtain a series of observations fitted for a continuation of the studies on the spectra of the elements, of which the commencement has been published in my "Recherches sur la constitution des spectres linéaires des éléments chimiques" (*K. Svenska Vetensk. Akad. Handl.* Bd. xxiii. No. 11), a spectroscope with one of Prof. Rowland's concave gratings (10,000 lines to the inch) was procured for the Physical Institution of the University of Lund. It was mounted in a most excellent manner by the Mechanician of the Physiological Institution, Hilding Sandström, according to the instructions of Prof. Rowland (*see* Ames, Johns Hopkins University Circulars, viii. No. 73, May 1889; Phil. Mag. [5] xxvii. p. 369), but with full freedom in the details of construction. The adjustments also were executed according to the same instructions, but

* See my work for Naphthalene in American Journal, xlii. p. 144, *et seq.*, 1891.

† Communicated by the Author.

with greater precision in the special determinations with the intention to obtain by the exactness of the adjustment the same scale through the whole spectrum.

However, when all adjustments were completed, no distinct image could be obtained in any part of the spectrum. In the visible spectrum of the first order the image was not very much out of focus, but the deviation increased gradually, so that it became necessary to displace the eyepiece several centimetres to obtain well-defined images of the spectra of higher orders. All details being executed with the same accuracy, there was nothing that could indicate the cause of the discrepancy, so that nothing remained but to make all the adjustments over again, determining at the same time the extreme limits of the errors. For this purpose I have made use of new methods of adjustment, and I have ascertained by these researches:—

1. That the courses which the apex of the grating and the cross hairs of the eyepiece follow in their movement on the rails do not deviate in any point from straight lines by more than 0·2 millim.

2. That the angle formed by the average directions of the rails did not differ from a right angle by more than 15″ (corresponding to an arc of 0·5 millim. at one of the ends of one of the rails), the difference probably not amounting to more than a third of this value.

3. That the middle of the slit could not be more than 0·2 millim. from the crossing-point of the lines that are described by the apex of the grating and the cross hairs of the eyepiece.

4. That the apex of the grating and the cross hairs of the eyepiece were not more than 0·1 millim. distant from the axes of the carriages.

5. That the distance between the centre of curvature of the grating and the axis of the carriage on which the eyepiece was placed, did not amount to 0·5 millim. during the whole movement.

6. That the lines of the grating and the direction of the slit were parallel and at right angles with the plane of the rails.

7. That the grating was entirely free from all constraint and of spherical form, the images in the centre of curvature being of excellent definition.

8. That the optical state of the slit was perfectly normal.

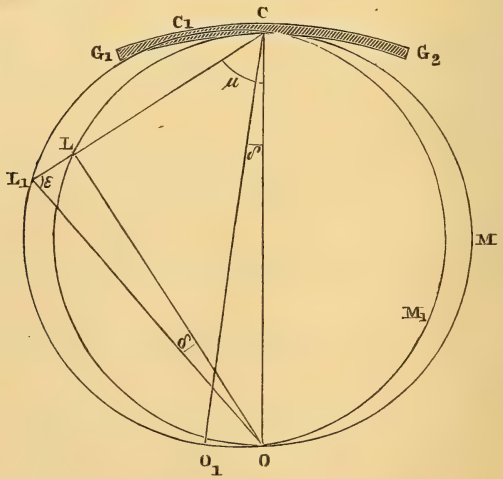
With these results it was only in the grating itself that the cause of the displacement of the spectra could be looked for, either in some imperfection of the theory or in some

fault in the execution of the work, at least with regard to the special grating in question. Hitherto, I had not deemed it possible to make any of these assumptions, as it seemed that Prof. Rowland himself and other spectroscopists who have used the concave gratings ought to have recognized such an anomaly, if it existed.

During all the adjustments the grating was left in the same position in its holder, so that I had made use only of the spectra on one side of the grating. Now it was removed from its holder and, after being reversed, it was adjusted in the same manner as before, with the intention of learning whether the focal curve that passes through the centre of curvature is symmetrical with respect to the principal axis of the concave mirror. Then it was found that the distance between the grating and the eyepiece ought to be increased in order to get distinct images, while before it was necessary to diminish it. From this it was evident that the inaccuracy in the position of the images was due to the grating.

II. First of all the question was to determine the true form of the focal curve that passes through the centre of curvature of the grating. According to Prof. Rowland's theory this ought to be a circle, which should have as a diameter the straight line that unites the centre of curvature with the apex of the grating. If the form of the curve differed perceptibly from a circle, it would not be possible with these gratings to obtain spectra of a uniform scale.

Fig. 1.



The form of the focal curve can be determined with the greatest facility, if the apparatus is altered in such a manner

that the slit is made movable along the rail that carries the grating.

Let G_1G_2 (fig. 1) be the grating, C its apex, O its centre of curvature, CLOM the theoretical focal circle, $CL_1O_1OM_1$ the true focal curve that passes through O, L the slit in its original place at the point of the right angle which is formed by the rails LC and LO. Then, on displacing the slit along LC or its elongation to a certain point L_1, it will always be possible to obtain distinct images of the spectra, supposing in all cases that such can be given by the grating. This point L_1 belongs to the curve in question, whose polar coordinates will be determined by measuring the radius of curvature CO (ρ), the displacement LL_1 (d), and the angle LCO (μ). For then, supposing d to be positive, when the slit is moved away from the mirror, the radius vector $L_1C = r = \rho \cos \mu + d$ and the vectorial angle $= \mu$.

Denoting the wave-length by λ, the number of order of the spectrum by n, the distance between two adjacent lines of the grating by ω, we should have, if the theory were exact,

$$\sin \mu = \frac{LO}{\rho} = \frac{n\lambda}{\omega}, \quad n\lambda = \frac{\omega}{\rho} \cdot LO.$$

To decide whether the same formula can be applied in the present case, it will be sufficient to displace the slit along the rail LC and to observe if any change is produced in the spectrum, viz., if the same value of μ always corresponds to the same value of λ independently of the value of r. In reality small irregular variations were found, which did not seem to exceed one of Ångström's units, and which were doubtless due to imperfections in the rails and the adjustment. According to the theory of concave gratings a difference of one Ångström's unit in the spectrum corresponds to a lateral displacement of the slit varying in the spectra of different orders between 0·25 and 1 millim. Consequently the formula is exact within the limits of error of our experiments. It follows that the angle ϵ of the segment CL_1O is determined by the equation

$$\cot \epsilon = \frac{d}{LO} = \frac{d\omega}{\rho . n\lambda}.$$

In this formula d and $n\lambda$ being the only variables, we see that it is sufficient that their quotient $\frac{d}{n\lambda}$ be constant, in order that the angle ϵ may be so too.

III. The measurements were executed in such a way that the spectroscope was directed on some known line of the

spectrum and the movable carriage that bears the slit displaced along the rail LC, until a distinct image was obtained in O. The position of an index, attached to the carriage, was read on a millimetre-scale fixed to the rail LC. Each of the numbers given in the following table under a_1 and a_2 is the mean of 10 of these readings, the carriage being alternately brought near to and removed from the grating. The column a_1 corresponds to the spectra on one side of the grating, the column a_2 to those on the other; a greater value denotes a greater distance from the grating. It was found that the slit could be displaced through the space of about one millimetre without it being possible to distinguish any variation in the definition of the image. The probable errors of the means amount in general to 0·2 millim., they never exceed 0·4 millim. Using as a source of light sometimes the sun, sometimes the voltaic arc, I directed the spectroscope in the spectra of the first four orders to the weak lines between D_1 and D_2 ($\lambda=5893$) and to the double lines b_3 and b_4 of the solar spectrum or the strong doublets of the neighbouring band of carbon (λ about 5165).

Spectral line.	Wave-length. $10^7 n\lambda$.	a_1.	a_2.	$\frac{1}{2}(a_1+a_2)$	Observed.		Calculated.
					d_1.	d_2.	d.
I. b_4...	1×5165	133·8	153·8	143·8	−10·0	+10·0	9·4
I. D...	1×5893	133·4	155·6	144·5	−10·4	+11·8	10·8
II. b_4...	2×5165	123·2	161·7	142·5	−20·6	+17·9	18·9
II. D...	2×5893	121·8	165·2	143·5	−22·0	+21·4	21·5
III. b_4...	3×5165	115·8	171·6	143·7	−28·0	+27·8	28·3
III. D...	3×5893	112·0	175·7	143·8	−31·8	+31·9	32·3
IV. b_4...	4×5165	106·0	181·6	143·8	−37·8	+37·8	37·7
IV. D...	4×5893	101·4	187·6	144·5	−42·4	+43·8	43·0
				Mean 143·8			

The first column contains the number of order of the spectrum and the line to which the spectroscope was directed; the second the approximate wave-length. In the fifth column are the means of the values of a_1 and a_2, which correspond to the same line in the spectra on the two opposite sides of the grating. These means approach, as we see, to a constant value 143·8, which corresponds evidently to the normal position of the slit at the vertex of the right angle formed by the rails. On determining by direct measurements this position, I have found $144{\cdot}8 \pm 0{\cdot}1$. But the difference of one millimetre between the two numbers is

perfectly explained through the uncertainty in the two adjustments of the centre of curvature of the mirror on the axis of the carriage of the eyepiece, first in the direction of the girder that unites the two carriages, and secondly, in the lateral direction. Of this I have convinced myself by another series of determinations, by displacing intentionally the centre of curvature. A fault of 0·5 millim. in the determination of the radius of curvature is sufficient to explain the before-mentioned difference.

Thus the point 143·8 is to be considered as the vertex of the right angle of the rails, through which passes in the present case the theoretic focal circle of the grating, or rather a curve which differs from it very slightly. Using this number (a_0) I have calculated the differences $d_1=a_1-a_0$ and $d_2=a_2-a_0$, which are found in the table under the heading "observed." A glance at these numbers shows that they are at least very nearly proportional to the corresponding values of $n\lambda$, which implies that the angle ϵ of the segment of the true focal curve is constant. To examine this more closely, we will insert in the preceding equation of ϵ

$$\frac{\rho \cot \epsilon}{\omega} = x,$$

and we will calculate by the method of least squares the exact value of x from the 16 equations of the form

$$x \,.\, n\lambda = d,$$

which we obtain from the preceding table on using all the values d_1 and d_2.

In this way we find the value

$$x = \frac{\rho \cot \epsilon}{\omega} = 18261 \pm 80.$$

The numerically equal values of d_1 and d_2, which are obtained on making use of this value of x, are given under d in the last column of the table. The differences between these numbers and the observed values being confined within the limits of errors of observation, it must be considered as proved that *the angle ϵ in the segment of the focal curve is a constant.*

A segment of which the angle is a constant belonging necessarily to a circle, we can express the result of our researches as follows:—

The focal curve which passes through the centre of curvature of the mirror is a circle, which, however, has not the radius of curvature in the apex of the grating as a diameter.

Always supposing, as in the preceding, that this curve also passes through C, we see on fig. 1 where CO_1 is a diameter of the true focal circle, that the angle between CO and CO_1 is $=\delta=\frac{\pi}{2}-\epsilon$.

We have then

$$\tan\delta=\cot\epsilon=18261\frac{\omega}{\rho}.$$

The determination of the radius of curvature has given $\rho=6434\pm1$ millim. According to the statement engraved on the grating, $\omega=0{\cdot}0001$ inch $=0{\cdot}00254$ millim. From this we obtain $\delta=24'\,47''$ and the arc $OO_1=\rho\tan\delta=18261\,\omega=46{\cdot}4$ millim. The difference between the diameters CO and CO_1 amounts to 0·17 millim.

IV. Though there could be no doubt as to the obliquity of the grating, it was possible that we had to do with some accidental anomaly peculiar to our special grating. For that reason it was of great interest for me to find an opportunity to examine another grating of the same kind, and this has been made possible through the kindness of Dr. A. E. Andersson at Kristianstad, who has been good enough to place at my disposal a concave Rowland grating of exactly the same kind as the preceding.

The measurements, which have been executed in the same order as before, follow here :—

Spectral line.	Wave-length. $10^7 n\lambda$.	a_1.	a_2.	$\frac{1}{2}(a_1+a_2)$	Observed.		Calculated.
					d_1.	d_2.	d.
I. b_4...	1×5165	130·3	155·6	143·0	−12·3	+13·0	11·6
I. D...	1×5893	129·2	158·5	143·9	−13·4	+15·9	13·2
II. b_4...	2×5165	118·3	164·6	141·5	−24·3	+22·0	23·2
II. D...	2×5893	115·5	168·7	142·1	−27·1	+26·1	26·4
III. b_4...	3×5165	108·6	177·4	143·0	−34·0	+34·8	34·8
III. D...	3×5893	104·2	181·1	142·7	−38·4	+38·5	39·7
IV. b_4...	4×5165	95·5	189·6	142·5	−47·1	+47·0	46·4
IV. D...	4×5893	89·7	195·3	142·5	−52·9	+52·7	52·9
Mean 142·6							

The probable errors of the values of a are a little greater than in the preceding case, and amount in maximum to 0·5 millim. Moreover the adjustments of the grating are not of quite the same exactitude, owing to the limited time I had at my disposal for making these determinations. Hence, there is nothing astonishing in the fact that the mean, 142·6, of the values of a differs a little more from the normal value,

144·8, than is the case with the other grating. The error necessary to produce such a difference does not exceed $\frac{1}{6000}$ of the distance to be determined.

On calculating as before the quotients $\frac{d}{n\lambda}$, we obtain

$$\frac{\rho \cot \epsilon}{\omega} = 22440 \pm 120.$$

The radius of curvature of this grating was found to be 40·3 millim. greater than that of the other, viz., 6474 millim., the uncertainty amounting to about 2 millim. With this value of ρ and the nominal value of ω, we find $\delta = 30' 16''$ and $OO_1 = 57{\cdot}0$ millim.

To judge from the inscriptions on the gratings the obliquity ought to have the same direction in both cases.

V. The focal curve that passes through the centre of curvature of the grating being a circle, as shown above, it will always be possible to adjust the spectroscope in such a manner as to obtain in all positions distinct images of the spectra without altering the distance between the grating and the eyepiece. It follows from the preceding that this is effected by causing the girder to act the part of the diameter O_1C of the true focal circle instead of that of a radius of curvature of the grating. Hence, in the first grating the girder ought to be lengthened by 0·17 millim., then turned round the point C through an angle $\delta = 24' 47''$. The easiest way of doing this is to displace the cross hairs of the eyepiece in O with the micrometer through a distance equal to the corresponding arc 46·4 millim. (to left or to right according to the side of the grating which we wish to make use of), and afterwards turning the grating until the cross hairs and their image coincide again. Then in all positions of the girder the slit ought to remain on the true focal circle. The exactitude of the theory and the measurements is confirmed by the fact, that after the execution of these adjustments the image became perfectly defined through the whole spectrum.

It would also be possible to obtain distinct images in all positions by another method, viz., by altering the angle of the rails by a quantity δ. In that case the centre of curvature ought not to be displaced, but it is necessary to turn the micrometer and the photographic box through an angle δ, so that they may be always tangents of the focal circle.

However, the supposition which we have made, that the true focal circle passes through the apex C of the grating, does not possess any very high degree of probability, because in that case the curve would intersect the surface of the

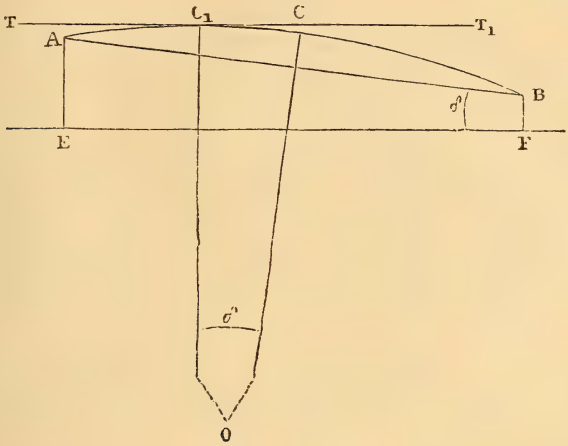
grating. It seems more likely that it touches it, but at another point, which, as can be seen by construction and calculation, would be situated at a distance of 46·4 millim. from the apex C. In reality, the conclusions that could be drawn from the measurements would remain almost the same, if we had replaced in fig 1 the circle $CL_1O_1OM_1$ by a circle passing through O but not through C or O_1 and touching the grating at C_1. This circle would have a radius equal to ρ, that is to say 0·17 millim. less than that of the former. As to the variation $\Delta\delta$ of the angle δ, we find $\sin \Delta\delta = \frac{\sin^2\delta}{2 \cos \mu}$, a quantity varying with μ, but which falls within the limits of errors of observation in all parts of the spectra, that we can use. The arc CC_1 differs from the arc OO_1 (46·4 millim.) only by some tenth of a millimetre. Under this new supposition an exact adjustment according to Prof. Rowland's theory is obtained by displacing the grating 46·4 millim. along its own surface, until the point of contact of the focal circle falls in with the axis of the carriage, where the apex of the grating was situated before. The considerable obliquity that the position of the grating would show in that case is the only difficulty with this arrangement. Hence I have preferred the first method of adjustment, after having convinced myself that the difference is of no importance from a practical point of view.

VI. On the other hand, the last manner of considering the matter seems to possess a considerable advantage, because it will allow us to account in a simple way for the relations between the true focal circle and the grating. In reality, the accordance with Prof. Rowland's theory is perfect and the obliquity is only due to the point of symmetry of the grating not coinciding with the apex of the concave mirror.

Let AC_1CBO (fig. 2) be a section through the centre of curvature, perpendicular to the surface A C B and to the lines of the grating. Let AB be the chord of the section, which is perpendicular to the radius CO that passes through the apex of the spherical cap. The lines of the grating being drawn perpendicular to the axis of the dividing-machine (and perpendicular according to our supposition to the plane of the paper) it will always be possible to draw in the plane of the paper a straight line EF parallel to the axis in question. On a tangent plane TT_1 to the spherical surface, parallel to EF and perpendicular to the plane of the paper, the dividing-machine would draw equidistant lines. On both sides of the point of contact C_1 of this plane the distances of the corresponding lines are also equal, C_1 is the point of symmetry and the point of contact of the focal circle. Then

it is immediately seen by the figure, that the angle which is formed by the straight lines AB and EF becomes equal to

Fig. 2.



the angle δ between the radii CO and C_1O. AB being = 150 millim. the values of the differences between AE and BF in the two gratings are found to be 1·08 and 1·32 millim. respectively.

In this way the asymmetry of the gratings is explained in a manner as simple as it is complete. However, the found differences being much greater than would be supposed in a work of such perfection as are the gratings of Prof. Rowland, we cannot exclude another hypothesis, the same that M. Cornu * has made use of in order to explain the focal properties of plane gratings, viz., a systematic variation in the distances of the lines. Such a variation would arise from an irregularity in the screw of the dividing-machine, and in the plane gratings this explanation seems to be the only one possible. But in the concave gratings the same fault might also arise from another cause. The two sides of the gratings giving spectra of different brightness, we may conclude that the furrows which the point of the diamond makes in the reflecting surface are not symmetrical in section. Then it is easy to see, that the distances of the lines are subject to a continual variation from one side of the grating to the other. But without knowing all details of work in the ruling of gratings, it would be useless to enter more closely into this hypothesis, and impossible to decide whether it is superior to the preceding.

* *C. R.* lxxx. p. 645.

XXIV. *Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge.* *By* E. C. C. Baly*.

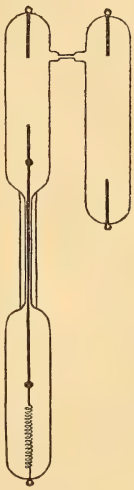
SOME time ago, on examining with a spectroscope a vacuum-tube which happened to contain a small quantity of hydrogen, during the passage of the electric spark I noticed that the hydrogen lines, while strongly visible in the negative glow, could not be seen in the body of the tube. The hydrogen appeared to be, in fact, withdrawn from the tube and collected about the negative pole. Finding the same result in a tube which I fitted up for the purpose, it appeared to me to point to a separation of the gases in the tube; and I determined to make a series of experiments with a view to investigating the matter and the behaviour generally of different gases under similar conditions.

The tubes I employed were about 9 inches long and $\frac{3}{4}$ inch internal bore. The electrodes were of aluminium wire, and, except in certain cases to which I shall refer, about $1\frac{1}{2}$ inch in length. Two of these tubes were connected to the pump at the same time, one direct and the other through tubes for the absorption of mercury vapour; so that in all the experiments results were obtained in the presence and in the absence of mercury vapour. Gas-generators, fitted with purifying and drying apparatus, were connected so as to allow of varying quantities of the particular gases under examination being admitted to the tubes as might be required. The pump, I may mention, was a modified form of the Geissler mercury-pump, to which I was able to attach an automatic apparatus for working it—a very great saving of labour. Measurements of the vacua were obtained by means of an ordinary barometer-gauge, and varied from 15 millim. to $\frac{1}{4}$ millim.

I first worked with varying quantities of carbon dioxide and hydrogen. On using certain mixtures of these gases exhausted to about $\frac{3}{4}$ millim., when the current was first passed a white glow appeared throughout the tube, no striæ being visible, giving a mixed spectrum of the two gases. After a few seconds the negative glow changed to a pink colour, and well-defined striæ, whiter than the preceding glow, began to appear. On watching this change with the spectroscope, the hydrogen lines in the tube were seen to become fainter and gradually to disappear, leaving only the spectrum of carbon dioxide, while those in the negative glow became

* Communicated by the Physical Society: read Feb. 10, 1893.

extremely brilliant. The current was then stopped, and the tube allowed to rest for about an hour, when, the current being passed again, the same phenomenon precisely occurred. Judging that if this were caused by actual separation of the two gases, it ought to be possible to fractionate out the hydrogen into another tube, I endeavoured for a long time unsuccessfully to do so; but at length succeeded by using a double tube of the shape shown in the figure. The longer of the tubes consisted of two chambers joined by capillary tubing, the smaller tube being connected to one of these by a narrow neck capable of being sealed off. Both tubes were furnished with electrodes. One of those in the large tube was sufficiently long to project through the capillary into the second chamber, and being connected at its base to the sealed platinum by a weak spiral wire could be dropped sufficiently far to touch the opposite electrode. This rod was made of copper, as being heavier than aluminium. It fitted the capillary fairly well, and was furnished with small stops of cotton-wool in order to close the capillary, and thus prevent as much as possible the diffusion of the gases. The tube, after being filled with the gases carbon dioxide and hydrogen, was exhausted and sealed from the pump. The copper rod was caused to touch the opposite electrode, and the current was passed so as to make the whole of the long tube the negative pole and the electrode at the lower end of the smaller tube the positive. The current was continued for a considerable time, when the connecting-neck between the tubes was sealed off and the copper rod shaken back to the stop. On comparing the spectra of the two tubes, it was found that the small tube (containing the positive pole) showed only a trace of hydrogen, while the other showed it brilliantly.



This, I think, may be considered a proof of an actual though not complete separation of the two gases.

I then tried hydrogen mixed with many other gases—amongst them nitrogen, carbon monoxide, sulphur dioxide, iodine, and mercury vapour; and in every case, without exception, I found that the hydrogen was collected about the negative pole in exactly the same manner as I have particularized.

I proceeded to examine mixtures of other gases. With carbon monoxide and carbon dioxide, the carbon monoxide is separated out and appears in the negative glow. With carbon dioxide and nitrogen the carbon dioxide is separated out, while the nitrogen remains in the tube, the separation being remarkably distinct. In this case it is the heavier gas which is separated out; and the same is found with carbon dioxide and sulphur dioxide, the sulphur dioxide appearing in the negative glow.

It would thus appear that the separation of two gases does not depend on their relative molecular weights. On examining a tube of air, however, the components of which are of fairly equal molecular weight, a separation was found to be very difficult, and only occurred after carrying the exhaustion to a much higher point than was usually necessary. The nitrogen remained in the tube, and the negative glow gave a spectrum presumably oxygen; I say presumably, for I am unable to see what else it can be. I was unable to produce the same spectrum in a tube with oxygen, but I was prevented from proceeding further. The spectra of oxygen Professor Schüster has shown to be very varied under different conditions. Is it not possible that the two spectra in an oxygen tube, the banded one in the negative glow, and the bright-line one in the rest of the tube, may be due to separation of two gases?

From these experiments it is evident that when the electric current is passed through a rarefied mixture of two gases, a process similar to electrolysis is set up, one of the gases being separated out and collected about the negative pole, the other gas remaining in the tube; the proof being that the gas separated out may be fractionated into another tube by the method I have above described. In pursuing these experiments I was struck by the apparent close connexion between separation and striation; that is to say, I found strongly marked striæ when there was good separation, and feeble striæ when the separation was difficult; I also found that the first appearances of these phenomena were coincident, the formation of striæ being always the sign of the commencement of separation. There were no exceptions to this, the action in all the tubes I made being the same.

It was evident to me that, if the connexion were real and the separation of the gases could in some way be prevented, by avoiding the negative glow, striæ would not be formed. I accordingly made a tube the negative pole of which did not protrude from the little glass collar in which it was placed, the positive electrode being made as usual. The tube was

filled with a mixture of hydrogen and carbon dioxide and exhausted. At a pressure of 24 millim. the current was passed ; instead of a negative glow appeared a little bunch of light about $\frac{1}{8}$ inch below the negative point. If this bunch of light impinged on the side of the tube, the glass became strongly phosphorescent. At 4 millim. there was no bunch of light or negative glow ; there was no sign of any striæ, the tube giving a spectrum of hydrogen and carbon dioxide, and no evidence of separation. I then reversed the current ; immediately striæ formed, separation began and became well-marked.

I tried various mixtures of gases and always obtained the same result, viz., that when the negative glow was avoided by the use of the minute electrode point, neither striæ nor separation occurred, but in reversal of the current strongly marked striæ and good separation.

My next step was to experiment with a pure vapour, which, if my contention be correct, should not striate. It is known that a tube of pure mercury vapour does not stratify. I prepared a tube for the purpose, one end of which was connected with the pump and the other with a bulb containing mercury. After exhaustion, I strongly heated the tube and boiled the mercury, which thus distilled through the tube. On passing the current, as I expected, no striæ appeared, but simply a beautiful phosphorescence throughout the tube, giving a spectrum of pure mercury only. On ceasing to boil the mercury and allowing the tube to cool, a small quantity of other gas was necessarily drawn in from the pump. Immediately striæ began to appear, beginning at the end of the tube connected with the pump; the negative glow changed at the same time and gave a spectrum containing other lines in addition to those of mercury, thus strongly confirming my previous conclusion.

Thinking that possibly the absence of striæ might arise, not from the purity of the mercury vapour, but from its molecules being monatomic, I repeated the experiment with pure vapours of iodine, sulphur, arsenic, and mercuric iodide, which are not monatomic. The result was in each case precisely the same—the tube while heated showing no striæ, but on cooling both striæ and separation.

Wishing if possible to obtain a pure gas which did not stratify at *ordinary* temperatures, I made many attempts to prepare a tube of pure hydrogen. The nearest approach to success was with hydrogen prepared from pure caustic potash and aluminium. The gas was then absorbed by red-hot palladium, which was re-heated in the vacuum. On passing

the current, the tube showed an even phosphorescent light throughout, with a very faint line of the most delicate striæ, very difficult to distinguish. The striæ did not become any plainer on carrying the exhaustion to a considerably higher point. I think it may be safely assumed that a tube of perfectly pure hydrogen would not striate at all.

From the foregoing results I think the following conclusions may be drawn :—

First, that when an electric current is passed through a rarefied mixture of two gases, one is separated from the other and appears in the negative glow.

Second, that striæ are caused by the separation of the two gases, and do not occur in a single pure gas or vapour.

XXV. *Notes on some Recent Determinations of Molecular Refraction and Dispersion.* *By* J. H. Gladstone, *D.Sc., F.R.S.**

AMONG the various indices of refraction which have been published by different observers of late years, there are some which have led me to further studies bearing on the general relation of this branch of Physics to Chemical theory. The following notes relate to the new metallic carbonyls, the metals indium and gallium, sulphur, and to liquefied oxygen, nitrous oxide, and ethylene.

I. Metallic Carbonyls.

Messrs. Ludwig Mond and Nasini † determined the molecular refraction of nickel tetracarbonyl for the red ray of hydrogen (H_α) as 57·7, and the specific dispersion between the lines γ and α of hydrogen as 0·03475, which will give a molecular dispersion between those limits of 5·93. This indicates a very great refraction and an enormous dispersion.

Through the kindness of Mr. Mond I have been able to determine the refraction of two specimens of iron pentacarbonyl for several lines of the spectrum, with the following result. The second and third lines in the Table relate to the same specimen, the latter representing measurements taken in a very acute-angled prism, and under the most favourable circumstances for seeing the more refractive rays; nevertheless the spectrum was cut off so suddenly about the bundle of rays at G that I cannot be sure of the exact measurement, but think it differs little from the line γ of hydrogen.

* Communicated by the Physical Society: read Feb. 10, 1893.

† *Lincei, Rendiconti,* vii. 411.

Specimen.	Temp. C.	Sp. Gr.	μ_A.	μ_B.	μ_C.	μ_D.	μ_E.	μ_F.	μ_G.
I....	22°	1·460	1·5026	1·5076	1·5096	1·5180	1·5289		
II....	15·5	1·4705	1·5063	1·5117	1·5146	1·5224	1·5329		
II....	13·4	1·474	1·5071	...	...	1·5230	...	1·5446	1·5650

From these observations we obtain the following molecular refraction, $\frac{\mu-1}{d}P=R$.

Specimen.	R_A.	R_B.	R_C.	R_D.	R_E.	R_F.	R_G.
I.	67·47	68·14	68·41	69·54	71·00		
II.	67·48	68·20	68·59	69·63	71·03		
II.	67·43	...	...	69·54	...	72·42	75·13

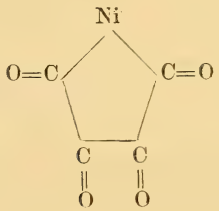
It is evident that in the iron compound also the refraction and dispersion are very great. The molecular refraction for the line α of hydrogen may be assumed at 68·5, and the molecular dispersion between the lines γ and α of hydrogen at 6·6. If we reckon for the lines A and H, we may assume H would be about 78·0, which would give a molecular dispersion between these limits of about 10·5.

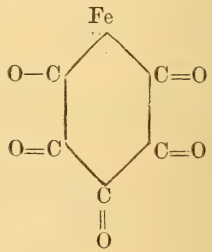
In discussing their observations, Messrs. Mond and Nasini, assuming that CO has a molecular refraction of 8·4, reckoned the atomic refraction of nickel at 24·1, instead of 9·9, which I had assigned to this element in solutions of its salts, and which subsequently has been fairly corroborated by Nasini's own experiments. This difference they attributed to a difference of valency in the metal. By parity of reasoning the atomic refraction of iron for the line C would be 26·5, or 25·5 for the line A, instead of 11·6 previously determined for bivalent iron from solutions of its salts.

But this involves the assumption that CO in these carbonyls has the same value as we should expect to find in an organic substance. It also assumes that the nickel has 8 valencies, while the iron has 10, in the above-named compounds, and that iron has presumably $\frac{7}{2}$ in diferrohepta-carbonyl; and that

potassium in its compounds with CO has still other valencies. There is also another difficulty; for if we determine the atomic dispersion of nickel and iron on the same principle, it will be found to be 4·8 and 5·2 respectively for the interval between the lines γ and a*; these numbers are about one fifth of the atomic refraction of the two metals given above, viz., 24·1 and 26·5. But the ratio between the atomic dispersion $(\gamma - a)$ and the refraction of the most dispersive elements hitherto calculated, sulphur and phosphorus, is only about one tenth.

It seems more probable that the metals really retain their ordinary valency, and that the excessive refraction and dispersion is to be sought rather in the peculiar arrangement of the CO. In such compounds we may imagine the CO playing a part similar to that of the CH_2 in ordinary organic compounds, which may be increased or diminished in number without altering the general type of the substance. In fact I accept on optical grounds as well as chemical, the ring-formulæ indicated in Mond's lecture at the Royal Institution.





In that case the molecular refraction due to each CO would be, from the nickel compound about 11·9, and from the iron compound about 11·3.

Although the atomic dispersion of nickel or of iron has not yet been definitely measured, it cannot greatly exceed 0·5 for $\gamma - a$. It is evident therefore from the figures for the dispersion, viz., $Ni(CO)_4 = 5·9$, $Fe(CO)_5 = 6·6$, that the molecular dispersion of each CO must be about the same in these two compounds, viz. 1·3, or thereabouts.

II. Indium and Gallium.

In 1885 I calculated the atomic refraction of indium and gallium from determinations of the refraction of certain alums made by M. Charles Soret. Very shortly afterwards

* Proc. R. S. xlii. p. 401.

he published another paper giving fresh and additional values for alums containing these metals *.

For indium the available data are derived from rubidium and cæsium indium alums, and for gallium from no fewer than five compounds, viz., potassium, rubidium, cæsium, thallium, and ammonium gallium alums. Calculated from these data, I find as mean values for the atomic refraction of these two metals the following :—

Metal.	Atomic Weight.	Specific Refraction.	R_A.
Indium	113·4	0·121	13·7
Gallium.....	69·9	0·166	11·6

These no doubt are nearer the truth then the higher figures previously given, though they must still be looked upon as only approximate. In regard to the atomic dispersion of these metals, the new observations quite confirm the previous remark that the order is "iron far the highest, chromium, indium, gallium, and aluminium lowest."

III. Sulphur.

In the following Table is given the atomic refraction of sulphur, either uncombined, or in very simple combination:—

Condition.	A.	C, or "red."	D, or "white."	F.	G or γ.	H.
Solid	.....	15·7	16·0			
Liquid	15·98	.....	16·47			
Gaseous	.....	16·1	.....			
In solution	15·5	15·7	16·0	16·7	17·3	
From CS_2	15·8	16·05	16·3	17·05	17·7	18·4
,, Cl_2S.....	.....	15·8	16·0			
,, Cl_2S_2	.....	15·9	16·1			
,, Br_2S_2	.....	16·35	.....			

Sulphur in the solid condition is deduced from the observations of Descloiseaux and other physicists; but as the crystals of sulphur give three different indices of refraction for the same ray, the arithmetical mean of these three indices has been simply taken as the basis of calculation.

Sulphur in a liquid condition is from the observations of

* *Archives Sc. Ph. & N. Genève*, xiv. p. 96.

myself and the late Pelham Dale. It agrees, as far as D is concerned, with a determination by Becquerel. $R_E = 16{\cdot}86$.

Sulphur in the gaseous condition was determined by Le Roux in 1861. The specific refraction was calculated out by me shortly afterwards, and recently by Nasini and Costa*. I give their number for the atomic refraction in the Table.

The sulphur in solution is from five determinations of this element dissolved in carbon bisulphide which I made some years ago with another object, and which have never been published. The solutions contained from about 22 to 27 per cent. of sulphur. Two determinations of somewhat weaker solutions were lately published by Nasini and Costa, and were practically identical with mine. The refraction of 17·3 for the line γ is deduced from their figures alone.

The four last lines give the values of sulphur reckoned from its simplest compounds.

In the case of bisulphide of carbon the figures in the Table are derived from my own most recent observations, which agree closely with those of other observers. The deduction made for the atom of carbon is 5·0 for the line A, 5·26 for the line H, and proportional numbers for the intermediate lines.

In the case of bichloride of sulphur the calculations have been made from the observations of Costa ; and in that of chloride of sulphur from those of Haagen, Becquerel, and Costa, which fairly agree. The refraction due to an atom of chlorine is assumed to be 9·95 for the line C, and 10·05 for the line D. Costa, in treating of these substances, has adopted a slightly smaller value for chlorine.

In the case of the bromine compound the sulphur is calculated from Becquerel's observations, taking the value for bromine at 15·35.

The figures for sulphur derived from these various sources are very similar. I doubt, however, whether the sulphur dissolved in bisulphide of carbon and the sulphur which forms part of that compound do exert exactly the same influence upon the rays of light. If we were to reckon the value of carbon in bisulphide of carbon by deducting the value found for sulphur in solution, we should get for A, $36{\cdot}6 - 31{\cdot}0 = 5{\cdot}6$, a higher figure than we ever find for carbon in a saturated compound. The difference would be still greater if reckoned by Lorenz's formula.

The accordance of the dispersion as exhibited throughout the Table is worthy of notice.

From the elaborate paper of Nasini and Costa, already referred to, it would appear that in some organic compounds,

* *Universita Inst. Ch. Roma*, 1891.

such as the xanthates, sulphur has at least the value of 16·0; but in the large majority of cases it has a distinctly lower value. In its oxygen compounds it is known to be far less refractive and dispersive.

IV. Liquefied Oxygen, Nitrous Oxide, and Ethylene.

In the recent paper of Professors Liveing and Dewar (Phil. Mag., Aug. 1892) they give determinations of the specific refraction of liquefied oxygen, nitrous oxide, and ethylene. It is, of course, possible to compare these interesting results with what theory would have led us to expect. The authors have themselves done so in the case of liquid oxygen at its boiling-point of $-182°$ C. They remark that the refraction-equivalent, 3·182, which they found, differs but little from that deduced from gaseous oxygen at the ordinary temperature, viz. 3·0316, and "corresponds closely with the refraction-equivalent deduced by Landolt from the refractive indices of a number of organic compounds," which was 3·0. It actually comes between the two values, 2·8 and 3·4, which were assigned by Brühl to oxygen in its different states of combination with carbon, and to which an intermediate value has since been added.

Liveing and Dewar were able to determine the refraction of liquefied nitrous oxide for six different wave-lengths, the extremes being the red ray of lithium and G. These gave for $\frac{\mu-1}{d}$ 0·2595 and 0·2691 respectively, and for the molecular refraction of the red ray 11·418, and of G 11·840. The molecular dispersion between G and the lithium-line is therefore 0·422, which would indicate about 0·63 between H and A. Now it is difficult to say what the rational composition of nitrous oxide is, and therefore what its theoretical refraction and dispersion should be. Nitrogen in ammonia and its congeners is reckoned at 5·1, in nitriles at 4·1; oxygen double-bonded is reckoned at 3·4, with two separate bonds at 2·8. We therefore, according to our theoretical views, might reckon nitrous oxide at 13·6, 13·0, 11·6, or 11·0. The probability is therefore clearly in favour of the lower figure for nitrogen. As the dispersion-equivalent of nitrogen in ammonia is as high as 0·38, this would also seem to exclude the idea of the nitrogen in nitrous oxide being in the same condition as in ammonia. This will probably be considered the most likely alternative also on chemical grounds.

On calculating Messrs. Liveing and Dewar's numbers for liquid ethylene, we obtain the molecular refraction of 17·2 for

the line D. But Professor Dewar has kindly furnished me with a more recent determination of what he believes to be a purer specimen. The refractive index, at the boiling-point, for the line C is 1·3445, and for the line F is 1·3528, the specific gravity being 0·55. These figures give 17·53 as the molecular refraction for the line C, and 17·92 for the line F. These will indicate about 17·41 for the line A. The theoretical value for ethylene, for the line A, is 17·4.

C_2	= 10·0
H_4	= 5·2
Double-linking . . .	= 2·2
	17·4

The coincidence between experiment and theory is very striking.

XXVI. *High Resistances used in connexion with the D'Arsonval Galvanometer.* By Frederick J. Smith, *Millard Lecturer in Mechanics, Trinity College, Oxford**.

THE great utility of the D'Arsonval galvanometer for determining current by the fall of potential method must have been felt by all who have used it for this purpose. When the instrument is thus applied, a large resistance is required in the galvanometer circuit. This is usually made of wire, and costs much. In 1890 I read a short paper before the Ashmolean Society of Oxford on the subject of resistances made of non-metallic substances and mercury jet-contacts.

Since then resistances of this kind have been constantly in use in the Millard Laboratory, and they have proved themselves to be both reliable and constant. They are made thus: Dry plaster of Paris and electrotype plumbago are intimately mixed together in suitable proportions†, the composition is then rammed tightly into a glass tube furnished with a platinum terminal; when nearly full another terminal is introduced and fixed in the substance by compression; the end of the tube is then closed over the wire in the blowpipe flame, and the resistance is finished.

In one resistance thus made the glass tube is 10 centim. long and 0·4 centim. in internal diameter, and has a resistance of about one megohm. Very finely powdered glass mixed with plumbago makes a good composition for high

* Communicated by the Author.

† Equal quantities of each in a tube 0·4 centim. diameter and 11·5 centim. long gave a resistance of 65,000 ohms.

resistances, but it is not so easily manipulated as the plaster and plumbago. Out of a large number of different substances tried, I find these two the most reliable. A megohm made by the method I have described costs only a few shillings.

Since October 1888 a D'Arsonval galvanometer has been in constant use here, in combination with a photographic apparatus, whereby a cylinder carrying bromide paper is constantly exposed to the reflected light from the galvanometer which shines through a long narrow slit placed in front of the revolving cylinder; by this means a constant record is kept of the current in a certain circuit. When the resistance of the galvanometer circuit is very high, the dead-beat action of the instrument is somewhat affected. I find that if a few turns of fine covered copper wire are wound on the outside of the rectangular coil of the instrument so as to form a closed circuit, it gives the same reading as before for a given potential difference, and is perfectly dead-beat in its action, so that with the addition of this damping-coil any amount of resistance may be used in the circuit of the galvanometer.

Trinity College, Oxford,
Feb. 10, 1893.

XXVII. *The Laws of Molecular Force.* *By* William Sutherland, *M.A.*, *B.Sc.**

In my last paper on this subject (Phil. Mag. April 1889) it was shown that if the law of force between two similar molecules is $3Am^2/r^4$, the parameter A could be calculated for a large number of bodies from Robert Schiff's measurements of their surface-tensions, and a law was announced connecting the values of A with chemical composition; but as this law was affected with exceptions in the case of the organic bromides and iodides and the amines, and as the argument from surface-tension requires the introduction of a considerable number of assumptions, I felt that it was very desirable to secure some other means of finding A. It soon appeared that the only satisfactory plan would be to return again to the search for the true characteristic equation of fluids on the model of Clausius's virial equation, as I had found that not one of those hitherto advanced was capable of general application. Fortunately the experimental material now available is so abundant and so well placed that I was completely successful in the quest, in the more tedious parts of which I had the advantage of assistance from my brother.

* Communicated by the Physical Society: read Oct. 28, 1892.

Mr. John Sutherland. Amagat's exhaustive study of the compression and expansion of gases, along with Ramsay and Young's work on ethyl oxide, were the groundwork of the research.

As the true characteristic equations for fluids are the key to many chambers of molecular physics, I have been able to enter many of these, and especially to discover the true law of the parameter A without exception. To give an idea of the scope of these investigations free from detail, I furnish the following table of contents:—

1. Establishment of characteristic equation for compounds above the region of the critical volume, with proof that there is discontinuity in the liquefaction of compounds.

2. The same for the gaseous elements, with proof of continuity during liquefaction in their case.

3. Brief discussion of exceptional compounds such as the alcohols and ethylene.

4. Establishment of characteristic equation below the region of the critical volume, its main feature being the occurrence in it of the same internal virial constant as in the equation for the region above the critical volume.

5. A short digression on the general interpretation of Clausius's equation of the virial.

6. Consideration of Van der Waals's generalization that if each substance has its temperature, pressure, and volume expressed in terms of the critical values as units, one and the same law applies to all bodies; proof that this is true for elements and compounds separately, above the critical region, and approximately true below.

7. Five methods of finding the internal virial constant: first, from the expansion and compression of the substance as gas or vapour; second, from its expansion and compression as liquid; third, from its latent heat; fourth, from its critical temperature and pressure; fifth, from its surface-tension: all the methods being afterwards proved to give accordant results for a large number of compounds.

8. The fifth or capillary method treated in greater detail, with digressions on the Brownian movement and molecular distances.

9. Establishment on theoretical grounds of Eötvös's relation between surface-tension and molecular domain (volume).

10. Tabulation for a large number of bodies of the product of the square of the molecular mass by the virial constant determined by several methods, and verification thereby of the general principles preceding.

11. Establishment of the law connecting the virial constant

of a substance with its chemical composition. Definition of the Dynic Equivalent of a substance and determination of its value for several radicals.

12. Close parallelism between Dynic Equivalents and Molecular Refractions.

13. Return to the discontinuity during liquefaction of compounds, and proof that it is due to the pairing of molecules.

14. Brief discussion of the constitution of the alcohols as liquids.

15. Methods of finding the virial constant for inorganic compounds, including a theory of the capillarity and compressibity of solutions.

16. Tabulation of the product of the square of the molecular mass by the virial constant for inorganic compounds, and determination of the Dynic Equivalents of the metals in the combined state. Again a close parallelism between dynic equivalents and molecular refractions or refraction-equivalents.

17. Meaning of this parallelism ; general speculations as to the volumes of the atoms and their relation to ionic speeds.

18. Attempt to determine the velocity of light through the substance of the water-molecule.

19. Suggested relation between the change in the volume of an atom on combination and the change in its chemical energy.

1. *Establishment of the characteristic Equation for Compounds above the region of the Critical Volume,* with proof that there is discontinuity in the liquefaction of compounds.—Amagat established (*Ann. de Chim. et de Phys.* sér. 5, t. xxii.) that for gases $\partial p/\partial T$ is a function of volume only down to volumes near the critical, but that at lower volumes it begins to vary with temperature. Ramsay and Young (Phil. Mag. May 1887), while verifying the independence of $\partial p/\partial T$ on temperature above the critical volume for such bodies as ethyl oxide and the alcohols, sought to show that this independence continues right into the liquid state ; but, as a matter of fact, their temperature-range in the experiments below the critical volume is not great enough to decide the question one way or another. We shall see that in the case of compounds Amagat's conclusion is the correct one, while in the case of the elements Ramsay and Young's contention appears to hold. The conviction that $\partial p/\partial T$ becomes slightly variable with temperature below the critical volume was one reason that determined me to represent the behaviour of fluids by two equations merging into one another ; the one applying down to near the critical volume, the other below that.

Clausius's equation of the virial is to be our guide in studying $\partial p/\partial T$,

$$\tfrac{3}{2}pv = \Sigma\tfrac{1}{2}mV^2 - \tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma Rr,$$

where V is velocity and R is force between two molecules at distance r apart.

According to the law of the inverse fourth power, the double sum of the internal virial reduces to an expression varying inversely as the volume and independent of the temperature, as I have shown before (Phil. Mag. July 1887).

If we integrate Amagat's relation $\partial p/\partial T = f(v)$, we get

$$p = f(v)T + \phi(v);$$

and as in the perfect gaseous state $pv = RT$, where v being the volume of unit mass and T reckoned as temperature C. + 273°, R varies inversely as the molecular weight of the substance, we will write our equation in the form

$$pv = RTvf(v) + v\phi(v),$$

where we see that $v\phi(v)$ stands for the internal virial-term. If, then, according to the law of the inverse fourth power, the internal virial varies inversely as v, then $v^2\phi(v)$ ought to be constant. Now Ramsay and Young have carefully tabulated the values of $Rf(v)$ and $\phi(v)$ for different values of v in the case of ethyl oxide; so it is easy to tabulate $Rvf(v)$ and $v^2\phi(v)$, as we proceed to do in the following Table, where v is the volume of a gramme of ethyl oxide in cubic centimetres, and the metre of mercury is the unit of pressure. These units will be used throughout when we are dealing with experimental results involving pressures; but when necessary, for theoretical convenience, we will convert to absolute units.

Table I.—Ethyl Oxide.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	·842		3·3	1·758	2413
100	·912	5710	3·0	1·865	2366
50	·973	5190	2·75	2·013	2371
20	1·129	4554	2·5	2·30	2487
15	1·201	4302	2·4	2·42	2519
10	1·327	3908	2·3	2·56	2550
8	1·409	3661	2·2	2·73	2589
6	1·525	3308	2·1	2·95	2646
5	1·595	3047	2·0	3·19	2691
4	1·654	2656	1·9	3·54	2771
3·7	1·682	2534			

The critical volume of ethyl oxide is between 5 and 4; so that if $\partial p/\partial T$ does become variable with temperature below the critical volume, the values of $Rvf(v)$ and $v^2\phi(v)$, calculated for volumes below 5, on Ramsay and Young's assumption that even below the critical volume $\partial p/\partial T$ is independent of temperature, will be affected with an error of more or less importance; they may therefore be regarded as a first approximation only and are added for comparison.

The first point to notice in these numbers is that $Rvf(v)$ increases steadily from its limiting value ·842 in the perfect gas state to double that amount near the critical volume, while at the same time $v^2\phi(v)$ diminishes from its limiting value in the gaseous state to the half of it near the critical volume. This result would seem at once to contradict the law of the inverse fourth power; but we shall see in the sequel that, in compression down to the critical region, there is a process of pairing going on among the molecules and producing this departure from the requirements of the law of the inverse fourth power, uncomplicated by such a process.

It is to be noted that the limiting value of $v^2\phi(v)$ is difficult to determine experimentally, because $\phi(v)$, the quantity measured, tends to the limit zero. But while below volume 4, $Rvf(v)$ increases with increasing rapidity, $v^2\phi(v)$ remains almost stationary, it dips a little and then increases; but remembering that its values count only as first approximations, we may assume that $v^2\phi(v)$ attains near the critical volume a value which remains constant in the liquid state, and is about half of the limiting value for the gaseous state. Thus there is discontinuity in the passage from the region above the critical volume to that below (or, more briefly but less accurately, during liquefaction). We must note carefully that in the range of volume from 4 to 1·9, which is a large liquid range, $v^2\phi(v)$ remains constant, as it should according to the law of the inverse fourth power, now that the process of pairing is completed.

To represent $Rvf(v)$ I found the form $R\{1+2k/(v+k)\}$ to be efficient; it gives the limit 2R to the function when $v=k$; and as ·842 is the known value of R, each of the above tabulated values of $Rvf(v)$ yields a value of k, the mean value 4·066 having been adopted by me. The other function, $v^2\phi(v)$, proved no less amenable to simple representation, the form found to fit it being $lv/(v+k)$, which attains the value $l/2$ when $v=k$; and as the value of k is known, we can calculate from each tabulated value of $v^2\phi(v)$ a value of l, and again adopt the mean value 5514. Hence down to near the

critical volume we have the behaviour of ethyl oxide represented by the simple form of equation

$$pv = \mathrm{RT}\left(1 + \frac{2k}{v+k}\right) - \frac{l}{v+k}, \text{ with } k = 4{\cdot}066 \text{ and } l = 5514,$$

involving only the two constants k and l peculiar to ethyl oxide.

We will now compare a few values of the pressures, in metres of mercury, given by this equation with those found by Ramsay and Young.

TABLE II.

	Volume	100.	50.	20.	10.	6.
175° C.	Pressure, experiment.	3·500	6·620	13·88		
	Pressure, calculated.	3·538	6·634	13·78		
195° C	Pressure, experiment.	3·710	7·020	15 06	23·00	27·00
	Pressure, calculated.	3·719	7·021	14·90	22·99	27·44
280° C.	Pressure, experiment.	.....	.....	19·80	34·59	49·62
	Pressure, calculated.	.....	.....	19·69	34·28	49·00

The agreement is as close as can be looked for; because although Ramsay and Young measure volumes to within ·01 centim., and pressures to within 2 centim. of mercury, the quantities measured cannot be considered known with that degree of accuracy; for the discrepancies between their measurements and those of Perot (*Ann. de Chim. et de Phys.* ser. 6, t. xiii.), who made special determinations in a large globe of the saturation-volume of ethyl oxide at different temperatures, are greater than those in Table II. Accordingly it would be useless to seek a better empirical representation of Ramsay and Young's results than the above; and as we are chiefly interested in establishing our simple form of characteristic equation, we had better proceed at once to the consideration of Amagat's experiments on carbonic dioxide, practically identical with Andrews's, but more extensive. Amagat's unit of volume is $\frac{1}{3410}$ of that occupied by the gas at 0° and 1 atmosphere; taking the weight of a litre of the gas at 0° and 1 atmosphere as 1·9777 gramme, we can convert Amagat's data to the gramme and centim. as units. The following Table is arranged in the same way as Table I.:—

TABLE III.—Carbonic Dioxide.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	1·421		2·64	2·56	1661
7·34	1·92	2159	2·35	2·64	1566
(7·00)	(2·11)	(2500)	2·05	2·77	1482
5·14	2·13	2071	1·91	2·86	1441
(5·00)	(2·37)	(2400)	1·76	3·02	1430
3·67	2·31	1858			

(The bracketed numbers are introduced from Andrews.)

A glance at this Table shows the same facts to be in it as in Table I. The critical volume of CO_2 is somewhere about 2; and we notice that near this volume $Rvf(v)$ tends to double the value 1·421 in the gaseous state, while at the same point $v^2\phi(v)$ approaches a constant value about the half of what must from inspection be estimated as the upper limit of it. Both functions are accurately represented by the same forms as in the case of ethyl oxide with $k=1·762$ and $l=2773$. With these values the following pressures were calculated for comparison with experiment :—

TABLE IV.—Carbonic Dioxide.

	Volume	11·74.	8·8.	5·87.	3·67.	2·64.	2·20.
100° C.	Pressure, experiment.	39	49·8	69	96·8	124	143
	Pressure, calculated.	39·4	50·4	70	99	123	137
70° C.	Pressure, experiment.	34·5	43·7	58·8	79·5	95	105
	Pressure, calculated.	34·8	44·0	59·4	80·0	94	100
35° C.	Pressure, experiment.	29·7	36·5	46·4	55·8	61	63·6
	Pressure, calculated.	29·5	36·5	47·0	57·5	60	57·7

The agreement is quite satisfactory except at the lowest volume, which is near the critical; and I have shown (Phil. Mag. August 1887) that near the critical point in capillary tubes the relation of pressure to volume becomes fickle, the measurements of Andrews and Amagat differing from one another as much as experiment and calculation in Table IV. To illustrate this at higher volumes I introduced into Table III. a couple of Andrews's values of $Rvf(v)$ and $v^2\phi(v)$, from values of $Rf(v)$ and $\phi(v)$ calculated by Ramsay and Young (Phil. Mag. 1887), after conversion of Andrews's air-manometer indications to true metres of mercury. It will be seen that

Andrews makes $\partial p/\partial T$ a little larger than Amagat; and this being so, it is not worth while to seek for closer agreement than that in Table IV., at least at present.

We have, however, a sensitive means of determining whether the form and the values of the constants adopted truly represent the behaviour of CO_2 closely enough at high volumes,—namely, Thomson and Joule's and Regnault's experiments on the cooling of CO_2 when it escapes through a porous plug from under pressure (Phil. Trans. 1854–1862; *Mém. de l'Acad.* xxxvii.). Natanson (Wied. *Ann.* xxxi.) has repeated the Joule and Thomson experiments on CO_2 under the more favourable conditions afforded by the commercial sale of the fluid in large quantity and great purity, so that he has been able to measure not only the cooling effect for a given pressure excess, but also its variation with pressure. Taking all these experiments together, we have a delicate test for the equation at high volumes.

The most convenient expression for the cooling effect for our present purpose is

$$K_p \frac{d\delta}{dp} = \theta \frac{dv}{d\theta} - v\,;$$

where δ is the cooling effect, K_p is the specific heat at constant pressure, and θ is temperature on the absolute thermodynamic scale. In previous papers I took from Joule and Thomson's original investigation $\theta = T + \cdot 7^\circ$, not then aware that Sir W. Thomson, in his article "Heat" (*Encyc. Brit.*), had by a fuller discussion of all the experimental data proved $\theta = T$, and so removed the difficulty that the term $\cdot 7$ opposed to the harmony of the thermodynamic and molecular kinetic conceptions of temperature.

With our characteristic equation the cooling effect is, after the appropriate reductions, given by

$$K_p \frac{d\delta}{dp} = 2(l/RT - k) + p\{4(l/RT - k)(l/RT - 2k) - 2k(l/RT - 2k) - lk/RT\}/RT.$$

Within Joule and Thomson's range of pressure this can be reduced to

$$K_p \frac{d\delta}{dp} = 2(l/RT - k)\,;$$

and $d\delta$ can be made to stand for the integral cooling effect if dp stands for the integral excess of 2·54 metres of mercury, to which they reduced their results. The term in p will be

taken account of when we come to Natanson's results. From Regnault's data we have, in dynamical measure

$$K_p = 424(\cdot 187 + \cdot 00027\,t).$$

TABLE V.

(Cooling effect of CO_2 escaping through a porous plug under a pressure excess of 2·54 metres of mercury.)

Temperature C....	7°·4.	8°.	19°·1.	35°·6.	54°.	91°·5.	93°·5	97° 5
Th. and Joule ...	4·4	4·2	3·9	3·4	2·95	2·35	2·16	2·13
Calculated.....	4·4	4·4	4·1	3·7	3·4	2·7	2·7	2·6
Temperature C.	−25°	3°.	100°.					
Regnault	6·3	4·1	2·6					
Calculated.....	5·5	4·5	2·6					

The agreement is as good as possible if both sets of experiments are taken into consideration. But Natanson's result affords a more delicate test; he found that at 20° up to 25 atmospheres the cooling effect for a pressure excess of one atmosphere could be represented by

$$\frac{d\delta}{dp} = 1\cdot 18 + \cdot 0126\,p\,;$$

while the theoretical equation above gives

$$\frac{d\delta}{dp} = 1\cdot 23 + \cdot 012\,p,$$

which is practically identical with Natanson's. On account of the closeness of this agreement we obtain as an indirect conclusion, that the experimental work on CO_2 taken as a whole makes the absolute thermodynamic zero −273°, the same result as Sir W. Thomson has obtained for air and H in the article "Heat" (*Encyc. Brit.*), while for CO_2, using only Regnault's coefficient of expansion and Joule and his own cooling effects, he found −273°·9. Now that CO_2 is seen to be in harmony with the other two more perfect gases, the number 273 may be accepted definitely as the absolute temperature of melting ice.

The equation therefore applies accurately at high volumes, a fact which we can prove by another test, seeing that Amagat carried out a special research (*Compt. Rend.* xciii.) to determine the ratios of pv to $p'v'$ at different temperatures and up to values of p' about 8 atmospheres, v being double v'.

TABLE VI.

(Values of $pv/p'v'$ at high volumes for CO_2.)
($p=5{\cdot}7$ metres of mercury : $v=2v'$.)

Temperature C.	50°.	100°.	200°.	300°.
Amagat	1·0145	1·0087	1·0040	1·0020
Calculated.....	1·0156	1·0092	1·0026	1·0000

As the experiments are not free from liability to an error of 1 in 1000, the agreement is again close enough to prove the applicability of the equation at high volumes.

In the sequel it will be shown that this equation applies to the great majority of compounds, but meanwhile the only other experimental determinations similar to those already discussed for ethyl oxide and carbonic dioxide are Amagat's for H_2, O_2, N_2, CH_4, and C_2H_4; Roth's for SO_2 and NH_3 (Wied. *Ann.* xi.); Janssen's for N_2O (Wied. *Beibl.* ii.); and Ramsay and Young's on methyl and ethyl alcohol (Phil. Mag. Aug. 1887). Our form of characteristic equation applies to SO_2, NH_3, and N_2O successfully, but not to H_2, O_2, N_2, and CH_4, which require a still simpler type, the alcohols on the other hand requiring a less simple type. These are the values of k and l for SO_2, NH_3, and N_2O :—

	SO_2.	NH_3.	N_2O.
k . .	2·08	4·8	2·3
l . .	2740	22040	3420

with which the following pressures have been calculated for comparison with the experimental data, the latter being taken direct from air or nitrogen manometer without correction for departure from Boyle's law.

TABLE VII.

SO_2 at 99°·6.			NH_3 at 99°·6.			N_2O at 25°·1.		
v.	p exp.	p calc.	v.	p exp.	p calc.	v.	p exp.	p calc.
41·9	7·9	8·0	172	7·6	7·6	7·0	39·1	37·2
17·6	17·1	17·0	85·7	14·8	14·7	5·36	42 6	42·4
13·6	21·2	20·8	65·4	18·8	18·9	3·78	43·9	46·7
9·9	26·0	26·2	40·0	28·6	29·1			
At 183°.			At 183°.			At 43°·8.		
18·2	21·7	22·0	160	10·3	10·2	5·83	49·4	47·9
10·0	37·3	36·9	81·6	19·8	19·6	4·62	55·6	54·4
4·58	69·2	67·5	36·1	40·9	42·1	3·47	61·4	61·0
2·75	98·2	93·5	16·2	82·6	85·4	2·82	64·1	64·3

This comparison has been made only to show that the form is applicable to other bodies as well as to ethyl oxide and carbonic dioxide ; full confirmation of the form will come later on, in the study of many of its applications.

2. *Establishment of the Characteristic Equation for the Gaseous Elements,* with proof of continuity during liquefaction. —The simplest plan in the case of the gaseous elements will be to take nitrogen as typical and tabulate for it $Rvf(v)$ and $v^2\phi(v)$ from Amagat's experiments up to 320 metres of mercury.

TABLE VIII.—Nitrogen.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas	2·233		4·15	3·25	1188
9·22	2·63		3·69	3·40	1007
6·91	2·77	1197	3·46	3·44	982
5·76	3·08	1396	3·23	3·80	1250
4·61	2·94	809			

The values of $v^2\phi(v)$ are unsteady, because the departures from Boyle's law are so small that $\phi(v)$ cannot be determined with accuracy ; but it is clear enough that $v^2\phi(v)$ does not tend to diminish within the range of volume available, not a wide enough one, however, to convince us that there is a radical difference between the course of this function in elements and compounds. But if we adopt from this Table as it stands the only possible conclusion that $v^2\phi(v)$ is constant, we shall be able to justify it by its consequences. In contrast to the constancy of $v^2\phi(v)$ is the tendency of $Rvf(v)$ at low volumes to double its perfect gas-value.

In the case of H_2 and O_2 the two functions run a similar course to that for N_2, but it is a more unexpected fact that they also do the same for the compound methane, CH_4, as is shown in Table IX.

TABLE IX.—Methane.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	3·908		12·11	5·24	6900
32·3	4·16		10·09	5·43	6400
28·2	4·30	5600	8·07	5·95	6500
24·2	4·39	6200	7·27	6·47	7000
20·2	4·73	6900	6·46	6·80	6800
16·1	4·73	6200	6·05	6·73	6200

It is evident that we have here to do with $v^2\phi(v)$ as a constant,

that is with an internal virial varying inversely as the volume down to near the critical volume, and $Rvf(v)$ tending somewhere near that point to about double its value in the perfect gas state. The course of $Rvf(v)$ in these four gases is represented by the simple form

$$R\left\{1+\frac{k}{2}\Big/\left(v-\frac{k}{2}\right)\right\},$$

which attains the value 2R when $v=k$. Hence the characteristic equation down to $v=k$ is

$$pv=RT\left(1+\frac{\frac{k}{2}}{v-\frac{k}{2}}\right)-\frac{l}{v},$$

a form which I had already adopted for air (Phil. Mag. Aug. 1887). The following are the values for k and l :—

	H.	N_2.	O_2.	CH_4.	Air.
k . .	12·0	2·64	1·78	5·51	2·47[2·11]
l . .	41700	1175	851	6460	1110[910]

The values given in brackets for air are those previously found by me from Amagat's data (*Compt. Rend.* xcix.), but as these data are not carried to such high pressures as those for N_2 and O_2, I have calculated values for air by adding to four fifths of the values for N_2 one fifth of the values for O_2.

This equation is almost identical with that of Van der Waals, but it is a little simpler. It gives the following pressures for comparison with Amagat's experimental results :—

TABLE X.

Hydrogen. At 17·7° C.			Nitrogen. At 17·7° C.			Oxygen. At 14·7° C.		
v.	*p* exp.	*p* calc.	*v*.	*p* exp.	*p* calc.	*v*.	*p* exp.	*p* calc.
166·9	57·5	56·9	13·83	46	45·7	5·73	88·9	89·7
100·1	99	99	6·91	92	91	3·58	141	142
60·1	176	176	4·61	145	142	2·58	201	203
46·7	238	241	3·69	194	188	2·43	216	219
			3·23	223	226			
At 100° C.			At 100 C.			At 100° C.		
166·9	74·2	73·3	13·83	60	60·5	5·73	123	124
100·1	129	128	6·91	125	124	3·58	204	204
60·1	230	229	4·61	200	199	2·58	300	301
46·7	311	315	3·69	270	266	2·43	322	327
			3·23	320	323			

The experimental numbers for oxygen are taken from Amagat's data in the *Comptes Rendus*, xci.

The most delicate test we can apply to our form at high volumes is, in the case of air, to compare the calculated with the experimental Thomson and Joule cooling effect. When I did this with the previous equation for air ($k=2{\cdot}11$ and $l=910$), I assumed the difference ·7° to exist between the melting-point of ice on the thermodynamic and gas thermometers; but, as already pointed out, Sir W. Thomson having proved this difference not to exist, there must have been a compensation of errors in the application of the previous equation. Thomson's expression for the cooling effect, applied to our equation for air, becomes

$$K_p d\delta/dp = 2l/RT - k/2,$$

which gives the following calculated values :—

Cooling effects of air escaping through a porous plug into the atmosphere under a pressure excess of 2·54 metres of mercury.

Temperature C.....	7°·1.	17°.	39°·5.	92°·8.
Experiment . . .	·88	·86	·75	·51
Calculation . . .	·84	·80	·71	·55

The agreement is the closest to be looked for and proves the accuracy of our equation for air at high volumes.

At low volumes we can test the form for all the elementary gases and CH_4 by applying it to the calculation of the critical volume, pressure, and temperature in each case. To do this at the present stage we must assume that our form can be trusted to hold not only to the critical volume but also a little past into the liquid region, a legitimate assumption for the elements, where we have seen the internal virial varying inversely as the volume, and so giving a guarantee of continuity, but not legitimate for the compounds where discontinuity occurs. Then, applying James Thomson's idea of the passage from the gaseous to the liquid state, as precisionized by Maxwell and Clausius, we have the critical point determined by the conditions $\partial p/\partial v=0$, $\partial^2 p/\partial v^2=0$.

Along with the characteristic equation these lead to the following values:—critical volume $v_c=3k/2$; critical temperature $T_c=16l/27Rk$; critical pressure $p_c=4l/27k^2$,—to compare with the experimental values found by Olszewski for O_2 and N_2 (*Compt. Rend.* c.), by Wroblewski for air, and by Dewar for CH_4 (Phil. Mag. 1884, xviii.).

TABLE XI.

		H_2.	N_2.	O_2.	CH_4.	Air.
Critical Volume.	exper. ...	.....	3·4	2·5		
	calc.	.....	3·96	2·67		
Critical Temperature.	exper. ...	.....	−146	−119	−99·5	−140
	calc.	−229	−155	−127	−95	−149
Critical Pressure.	exper. ...	.....	27	38	37	30
	calc.	19	25	40	32	27

The agreement is all that can be looked for in view of the difficulties of measuring these low critical temperatures and their associated pressures. With regard to hydrogen all we know is that Olszewski (*Compt. Rend.* ci.) has submitted it to a temperature estimated by him as −220° without a sign of liquefaction. If our equation is to be trusted, it would indicate that he would need to go some 10 degrees lower before the only unliquefied gas is conquered. Wroblewski has published data on the compressibility of H_2 up to pressures of 70 atmospheres at temperatures of −103° and −182° (Journ. Chem. Soc. 1889), and with these our equation is in accord, but there is hardly need of tabulated proof.

3. *Brief discussion of exceptional Compounds* such as the Alcohols and Ethylene.—To complete our survey of the experimental material on bodies above the critical region we have to consider Ramsay and Young's observations on methyl and ethyl alcohol, and Amagat's on ethylene. Ramsay and Young point out that at low volumes the values of $\partial p/\partial T$ for the alcohols are not so reliable as for ethyl oxide, being determined from a smaller temperature range; hence our values of $Rvf(v)$ and $v^2\phi(v)$ are not so reliable as before, but they suffice to show the exceptional nature of these bodies.

TABLE XII.—Methyl Alcohol.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	1·950		25	3·50	24800
340	2·14		20	3·70	23000
240	2·32	45500	18	3·79	22000
200	2·40	48000	16	3·97	21700
170	2·46	46100	14	4·18	20900
135	2·56	43700	12	4·38	19900
100	2·70	41000	11	4·46	19000
70	3·04	42100	10	4·53	17900
50	3·10	33500	9	4·58	16700
40	3·20	30200	8	4·55	15000
30	3·37	26800	7	4·39	12900

Table XII. (*continued*).—Ethyl Alcohol.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	1·35		8	3·43	11300
108·2	1·65	18000	6	3·34	8600
53·4	1·83	15000	4	3·37	6200
30	2·16	15000	3	3·51	5000
26·1	2·31	16000	2·4	3·93	4600
18·2	2·83	17000	2	4·87	4700
12	3·32	15000	1·8	5·83	4900
10	3·41	13500	1·6	7·06	4900
9	3·43	12500	1·4	8·81	4700

The numbers for methyl alcohol do not extend as far as the critical volume, while those for ethyl alcohol go considerably beyond it, lying as it does between 3 and 4; but we notice in both cases that $Rvf(v)$ increases from the limiting gaseous value, but attains a practically constant value before the critical volume is reached. In ethyl alcohol we may say that the value 3·4 is retained from volume 10 to volume 3, and moreover this 3·4 is not now double the initial 1·35, but about 2·5 times it. In methyl alcohol the value 4·5 may be said to be retained constant from volume 11 to 7, the lowest on the table; so that it is probable that, as in the case of ethyl alcohol, this value will be retained down to the critical volume: here again, also, the 4·5 is more than double the initial 1·95, but is only 2·3, not 2·5, times it.

Note that, in ethyl alcohol, as soon as the critical volume is passed $Rvf(v)$ begins again to increase rapidly, just as happened in the case of ethyl oxide. But for our present purpose more interest attaches to the course of $v^2\phi(v)$. In methyl alcohol at high volumes it seems to approach a limit which we may assign as 46,000, and then at volume 16, where $Rvf(v)$ has risen to double its initial value, $v^2\phi(v)$ has fallen to almost half of 46,000, but as $Rvf(v)$ continues to rise $v^2\phi(v)$ continues to fall, and still continues to do so even when $Rvf(v)$ has become constant. In methyl alcohol we cannot follow the changes right down to the critical volume, but in ethyl alcohol we see that $v^2\phi(v)$ attains at the critical volume a value which is carried constant into the liquid state, this constant value being about one quarter of the apparent limiting value 20,000 at large volumes. The constancy of $v^2\phi(v)$ below the critical volume is in striking contrast to the rapid variation of $Rvf(v)$.

I have not sought to represent by formulas the course of the two functions for the alcohols, as I have doubts about

$\partial p/\partial T$ being independent of temperature in the case of the alcohols; if it is variable then the values of our functions are affected with error. In any case we have seen that above the critical region the alcohols behave differently from our two typical compounds, ethyl oxide and carbonic dioxide; in section 14 it will be seen that in the liquid region, on the other hand, the alcohols approach the regular compounds in many respects, but are still exceptional in others. There remains now only ethylene to consider as to its gaseous behaviour.

TABLE XIII.—Ethylene.

v.	$Rvf(v)$.	$v^2\phi(v)$.	v.	$Rvf(v)$.	$v^2\phi(v)$.
Perfect gas.	2·22		4·61	4·15	4500
20·75	2·71	5800	4·15	4·45	4500
16·14	2·78	5320	3·69	4·81	4400
11·53	3·07	5500	3·22	5·71	4700
9·23	3·24	5300	2·77	6·41	4400
6·92	3·58	5100	2·65	6·63	4200
5·76	3·83	4900	2·54	7·87	5000

According to Cailletet and Mathias (*Compt. Rend.* cii.), the critical volume of ethylene is about 4·5; so that again in the above table we see $Rvf(v)$ near the critical volume attaining double its initial value and increasing rapidly thereafter. Once more, too, we see $v^2\phi(v)$ attaining near the critical volume a value which it retains constant below; but ethylene is exceptional in that this value is not half the limit at high volumes. The facts in the above table may be summarized in the statements that $Rvf(v)$ may be represented by the form $R(1+k/v)$, and $v^2\phi(v)$ by the form $vl/(v+a)$; so that the characteristic equation for ethylene is

$$pv = RT\left(1+\frac{k}{v}\right)-\frac{l}{v+a},$$

with $k=4{\cdot}15$, $a=1{\cdot}64$, and $l=6270$.

The form for ethylene is intermediate in simplicity between that for the simple gases and that for compounds, except that it has an extra constant. It is also worth noting that the forms

$$\frac{k}{2}\Big/\left(v-\frac{k}{2}\right),\quad k/v,\quad \text{and}\quad 2k/(v+k)$$

are special cases of a general form

$$nk/\{v+(n-1)k\},$$

with $n=\frac{1}{2}$, 1, and 2.

4. *Establishment of Characteristic Equation below the region of the Critical Volume.*—Now that we have practically exhausted the available data of the gaseous state, we see that by themselves they do not give much scope for generalization; but if we can secure an equation applicable from the critical volume down to the volumes of liquids in the ordinary state, then, with two equations covering almost the whole range of fluidity, we shall have a much larger experimental area laid under contribution for information on the characters of molecules.

Already we have secured one important fact towards the acquisition of such an equation, namely that below the critical volume the internal virial term varies inversely as the volume; and in the case of ethyl oxide we know its actual amount $l/2v$ with $l=5514$. We have therefore only to add to $l/2v$ Ramsay and Young's values of pv at different temperatures for different volumes below the critical, and we obtain the values of the kinetic-energy term in the desired equation; we can then proceed to study how this quantity depends on temperature and volume, and express the resulting conclusions in a formula.

As to the form we have this clue, that it must join on continuously with the previous one where that ceases to be applicable. Now the first fact to notice is that our form for compounds above the critical region cannot, like that for the elements, give a critical point by itself at all; for given p and T it is not a cubic but a quadratic in v, and hence cannot give us the three equal roots which are adopted as characteristic of the critical point when we apply the conditions

$$\partial p/\partial v = 0, \quad \partial^2 p/\partial v^2 = 0.$$

This emphasizes the discontinuity in compounds as contrasted with elements. However, we know as an experimental fact that at the critical point $\partial p/\partial v=0$, which with the characteristic equation gives us only two relations between the critical temperature, pressure, and volume. As a third relation that would perfectly define these three quantities I was led to believe that the critical volume is proportional to k, and found that

$$\text{critical volume } v_c = 7k/6$$

is the relation which, with the two others, gives successfully the numerics of the critical state in agreement with experiment. As this will be proved subsequently (Section 10) for a large number of substances, I will not delay at present to give examples, except for those compounds for which we have already found k and l.

TABLE XIV.

Critical temperature, $T_c = 120\,l/409\,Rk$; critical pressure, $p = 36\,l/409\,k^2$.

		$(C_2H_5)_2O$.	CO_2.	SO_2.	NH_3.	N_2O.
Critical Temperature.	exper. ...	194	32	155	130	35
	calc.....	199	52	125	96	36
Critical Pressure.	exper. ...	27·1	59	60	87	57
	calc.....	29·3	78·6	56	84	57

The want of accuracy in the agreement in parts of this table is to be ascribed partly to inaccuracy in the ordinary determinations of the critical point, as I have already pointed out that capillary action must sometimes largely affect the numerics of the critical state when these are determined in capillary tubes (Phil. Mag. August 1887). Regnault, in his account of his experiments on the saturation-pressures of CO_2, expressly declares that he had liquid CO_2 at 42°, which is 10° above the apparent critical temperature in capillary tubes; and Cailletet and Colardeau (*Compt. Rend.* cviii.) have shown that although the meniscus between gas and liquid CO_2 disappears to the eye about 31° or 32°, yet characteristic differences between liquid and gas can be proved to exist several degrees higher than this. Hence an error of at least 10° is possible in ordinary determinations of critical temperatures. On the other hand, an error of 5 per cent. in the value of an absolute temperature of about 400° as given by our equation would amount to 20°. Table XIV. is to be taken in the light of these facts.

We have now ascertained a second property that our equation for volumes below the critical is to possess: it must begin to apply when $v = 7k/6$, as the other form cannot apply below this volume at the critical temperature. At this volume the kinetic-energy term in our form above the critical region becomes

$$RT(1+12/13), \quad \text{or} \quad 25RT/13;$$

so that 25R/13 is the lower limit of the term which in the new equation is to take the same place as $Rvf(v)$ hitherto. Hence for this term the form

$$25R(1+F(v))/13$$

naturally suggests itself, and as $F(v)$ is to vanish when $v = 7k/6$, we get $(7k/6 - v)/\psi(v)$ as a suggestion for its form; and it only remains from the data obtained, as I have said, by

adding $l/2v$ to Ramsay and Young's values of pv for volumes of ethyl oxide below k, to determine the form of the function $\psi(v)$. This was found, after a rather tedious search, to come out in the simple form

$$\sqrt{T}(v-\beta)/B\ ;$$

so that finally we have the following as the equation for ethyl oxide below the volume k:

$$pv = R'T\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)-\frac{l}{2v},$$

with the following values for the constants:

$$R'=25R/13,\quad k'=7k/6,\quad B=63{\cdot}1,\quad \beta=1{\cdot}11,$$

R, k, and l as before.

I propose to call this the infracritical equation. It is to be noticed that we have introduced only two additional constants; so that, as regards number of constants, we could hardly look for a simpler form.

Above the volume $7k/6$ the appropriate form was proved to be

$$pv = RT\left(1+\frac{2k}{v+k}\right)-\frac{l}{v+k},$$

which I propose to call the supracritical equation.

Between k and $7k/6$ we have the circacritical form

$$pv = R'T\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)-\frac{l}{v+k}.$$

This, then, gives the complete representation of ethyl oxide in the fluid state if we establish the sufficiency of the infracritical form, as we now proceed to do. In the next table are compared the pressures found by Ramsay and Young and those given by the equation.

TABLE XV.—Liquid Ethyl Oxide.

Volume		3·7.	2·75.	2·25.	2.	1·9.
195° C.	Pressure, exper. .	28	29	43		
	„ calc. ...	32	26	45		
175° C.	Pressure, exper. .	.....	.....	19	43	
	„ calc. ...	.....	.....	14	48	
150° C.	Pressure, exper. .	.....	.....	.....	.....	19·5
	„ calc. ...	.....	.....	.....	.....	20

For the proper appreciation of this table it must be borne in mind that as soon as we enter the liquid region the pv term of the characteristic equation becomes the small difference of two terms, a small percentage error in either of which becomes a large one in pv. The fact that the above table brings out is that from 150° to 195° the relation between volume and temperature given by the equation is so accurate as to make only the small errors in pressure in the above table. But to show this more directly, we will now compare the volumes of the liquid under a pressure of 9 metres of mercury between 0° and 100°, as determined by Grimaldi (Wied. *Beibl.* x.) and as given by the equation. The specific gravity of ethyl oxide at 0° and under one atmosphere is taken as ·7366.

TABLE XVI. ($p=19{\cdot}5$ metre.)

Temperature	0°.	50°.	100°.	150°.
Volume, experiment.....	1·355	1·469	1·630	1·9
„ calculated	1·354	1·467	1·633	1·9

This, taken in conjunction with Table XV., shows that the equation represents with a high degree of accuracy the expansion of liquid ethyl oxide right up to the critical volume. It is now to be tested as to its power to give compressibilities correctly. The next Table contains the calculated compressibilities of liquid ethyl oxide, and also the experimental as given by Amagat (*Ann. de Chim. et de Phys.* 5 sér. t. xi.), Avenarius (Wied. *Beibl.* ii.), and Grimaldi (Wied. *Beibl.* x.). Amagat's values had to be interpolated for comparison with the others.

TABLE XVII.

Compressibilities with metre of mercury as pressure-unit.

Temperature	0°.	40°.	60°.	100°.
Amagat	·000200	·000309	·000380	·000730
Avenarius	·000178	·000317	·000403	·000654
Grimaldi	·000207	·000316	·000407	·000632
Equation	·000183	·000300	·000392	·000710

The agreement here is again satisfactory, and we have now seen that our form, with only two constants in addition to those characteristic of the gaseous state, can give both the expansion and compression of the liquid at low pressures; but Amagat has measured these also at high pressures up to 2000 and 3000 atmos. (*Compt. Rend.* ciii. and cv.), and the following Table compares first his values of the mean coefficient of expansion between 0° and 50° at pressures from 76 up to 2280 metres with those given by the equation, and, second, his values of the mean compressibility at 17°·4 and at pressures up to 1500 metres with those given by the equation. If v_1 and v_2 are the volumes at p_1 and p_2, then the mean compressibility is taken as $(v_1-v_2)/v_1(p_2-p_1)$. The apparent compressibilities given by Amagat are converted to true values by adding ·000002, which he has since given as the compressibility of glass.

TABLE XVIII.

Mean Coefficient of Expansion at high pressures.

p in metres ...	76.	380.	760.	1140.	1520.	1900.	2280.
Amagat	·00170	·00112	·00091	·00077	·00070	·00063	·00056
Equation	·00170	·00101	·00076	·00066	·00056	·00050	·00047

Mean Compressibilities at high pressures.

p in metres ...	76 to 114	114 to 366	366 to 654	654 to 933	933 to 1218	1218 to 1500
Amagat	·000208	·000143	·000112	·000086	·000070	·000062
Equation	·000197	·000128	·000085	·000060	·000046	·000037

As regards expansion the equation goes fairly near to the truth; except at the lowest pressures, it gives coefficients somewhat smaller than the experimental, but it parallels closely the main phenomenon of the rapid diminution of the coefficient with rising pressure. But in the compressibilities there is an increasing divergence between experiment and equation with increasing pressure, although again the equation is true to the main fact of the rapid diminution of compressibility with increasing pressure. We may conclude from the last table that our equation holds within the limits of experimental accuracy up to 760 metres; beyond that it begins to fail. A simple empirical modification would adapt the form to the whole of Amagat's range, but as it stands it will be found good enough for our applications.

We will now consider briefly how this form applies to carbonic dioxide below the critical volume; and the comparison

is interesting, as it relates to temperatures both above and below the critical. The values of the constants are B=54, β=·692.

TABLE XIX.

Carbonic Dioxide below critical volume.

Volume		1·526.	1·203.	1·115.	1·027.
70° C.	Pressure, exp.	150	274		
	„ calc.	152	266		
35° C.	Pressure, exp.	69	126	187	320
	„ calc.	69	120	184	320
18° C.	Pressure, exp.	.....	.....	99	200
	„ calc.	.....	.....	97	208

The agreement is within the limit of experimental error at the high pressures. Cailletet and Mathias have determined (*Compt. Rend.* cii.) the density of liquid CO_2 at various temperatures under the pressure of saturation. Here is a comparison with a couple of their results :—

	Temperature	−34°.	0°.
Volume—	Cailletet and Mathias	·946	1·087
„	Equation	·943	1·086

As far as compound gases are concerned, the applicability of the form for volumes below the critical has now been demonstrated in two typical cases. The elementary gases have now to be considered as to their behaviour below the critical volume. The data are again those furnished by Amagat (*Compt. Rend.* cvii. and Phil. Mag. Dec. 1888) on the compressibility of these gases between 760 and 2280 metres of mercury. Our study of these bodies above the critical volume has given us the knowledge that the internal virial term below k must be l/v, and the kinetic-energy term at the critical volume is 3RT/2, and with these guides the complete form required is soon found from the experimental numbers. It is

$$pv = \tfrac{3}{2}\mathrm{RT}\left(1+b\,\frac{\frac{3}{2}k-v}{v-\beta}\right)-\frac{l}{v},$$

with the following values for the additional constants β and b :—

	k.	β.	b.
Hydrogen	12	4·3	·480
Nitrogen	2·64	·81	·420
Oxygen	1·78	·604	·4415
Methane	[5·51]	[1·59]	[·447]

The approximate equality of the values of the constant b is worth noting. I have also reproduced here the values of k at the side of those for β, in order to point out that β is nearly $k/3$ in each case. Amagat has not published data for methane at volumes below the critical region, but the numbers given in brackets for methane were obtained indirectly as explained below. These relations of β and b give our equation such a degree of simplicity as largely to establish the soundness of its form. The next Table shows the degree of accuracy with which it represents the experimental facts.

TABLE XX.—Oxygen at high pressures.

Volume		1·277.	1·097.	1·008.	·949.	·905.
15° C.	Pressure, exp.....	760	1140	1520	1900	2280
	„ calc. ...	739	1141	1512	1893	2296

The agreement is quite as good for hydrogen and nitrogen.

By means of this equation we can calculate the volumes of a gramme of liquid nitrogen and oxygen at their boiling-points under a pressure of ·76 metre, for comparison with Wroblewski and Olszewski's determinations of the same (*Compt. Rend.* cii.; Wied. *Beibl.* x.; and 'Nature,' April 1887).

		Oxygen.		Nitrogen.
Volume at −184°	Wroblewski . .	·85	at −194°	1·20
	Olszewski . .	·89		1·13
	Equation . ·	·90		1·26

The equation is seen to give the volumes of these two bodies at these low temperatures within the present limits of experimental accuracy, and accordingly it covers a range of 2000-metres pressure and almost the whole experimental range of temperature. In the case of methane, if we take Olszewski's value 2·41 for its volume at −164°, and assume b is the mean of b for H_2, N_2, and O_2, then we can calculate the value of β which is tabulated above.

To ethylene above the critical region we had to assign a special form intermediate between that for ordinary compounds and that for elements; so that we had better do likewise for its infracritical equation, which I have cast in the form

$$pv = (1+\tfrac{4}{5})\mathrm{RT}\left(1+\frac{\sqrt{\mathrm{T}}}{\mathrm{B}}\cdot\frac{\frac{5}{4}k-v}{v-\beta}\right)-\frac{l}{v}\cdot\frac{k}{k+a},$$

with $B=56{\cdot}5$, $\beta=1{\cdot}53$. For the elements we had $v_c=3k/2$, for ordinary compounds $v_c=7k/6$; so that to make ethylene intermediate v_c is taken as $5k/4$, all these being of the general form $(1+2n)/2n$, with $n=1, 2, 3$.

With the values of the constants B and β given above as derived from Amagat's results at high pressures, we can determine the density of liquid ethylene; at $-21°$ under saturation-pressure the density is ·414, identical with the experimental value of Cailletet and Mathias (*Compt. Rend.* cii.).

It will be as well at this stage to extract clear from among the argumentative detail the most important results so far obtained.

First, in the elements the internal virial varies inversely as the volume over the whole experimental range.

Second, in compounds there is mathematical discontinuity in the value of the internal virial at volume k; from volume k downwards the internal virial varies inversely as the volume: from the volume k upwards it tends towards variation inversely as the volume as the limiting law, the limiting constant being double that which holds below the volume k; between the two limiting cases the internal virial of compounds varies inversely as $(v+k)$.

Third, a fact of the highest importance in connexion with the kinetic-energy or temperature term in the equation arrests our attention, namely, that the coefficient of T in it, or the apparent rate of variation of the translatory kinetic energy with temperature at constant volume, attains near the critical volume double its value in the gaseous state, and below the critical region increases rapidly with diminishing volume (see column $Rvf(v)$ in Table I.), becoming at ordinary liquid volumes as much as ten times as large (see coefficient of T in infracritical equation). Now the specific heat of liquids at constant volume, which is the rate of variation of the total energy with temperature, is rarely much more than twice that for their vapours. Hence we must seriously consider the interpretation to be put on the different terms of our equations.

5. *A short digression on the general interpretation of Clausius's Equation of the Virial.*—Returning to Clausius's theorem of the virial,

$$\tfrac{3}{2}pv = \Sigma\,\tfrac{1}{2}mV^2 - \tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma\,Rr,$$

we see that strictly the kinetic-energy term includes not only the energy of the motion of the molecules as wholes, but also that of the motion of their parts, and at the same time the

internal virial includes the actions between the parts of the molecules as well as those between the molecules. Calling these actions the chemic force, we can write the theorem thus:

$\frac{3}{2}pv$ = the total kinetic energy—chemic virial—virial of molecular forces.

Now in the usual treatment of the equation it is assumed that the chemic virial is equal to that part of the total kinetic energy which is due to the motion of the parts of the molecules relatively to their centres of mass, and neutralizes it in our equation, reducing it to

$\frac{3}{2}pv$ = translatory kinetic energy of molecules as wholes —virial of molecular forces.

But if we retain the full equation, and assume that the virial term we have been finding for various bodies is the true virial of the molecular forces, and includes none of the chemic virial, then the term usually regarded as the translatory kinetic energy of the molecules as wholes is really the total kinetic energy minus the chemic virial.

Let E be the total kinetic energy of unit mass, V the virial of the chemic forces, and P their potential energy; then, above the critical volume,

$$E-V=\tfrac{3}{2}RT\left(1+\frac{2k}{v+k}\right)$$

and

$$\frac{\partial}{\partial T}(E-V)=\tfrac{3}{2}R\left(1+\frac{2k}{v+k}\right),$$

which in the limiting gaseous state becomes 3R/2.

Also

$$\frac{\partial}{\partial T}(E-P) = K_v,$$

the specific heat at constant volume.

Below the critical volume,

$$E-V=\tfrac{3}{2}R'T\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right),$$

$$\frac{\partial}{\partial T}(E-V)=\tfrac{3}{2}R'+\tfrac{9}{4}R'\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta};$$

and, again,

$$\frac{\partial}{\partial T}(E-P) = K_v.$$

Now we can calculate K_v from the experimental values of K_p by the relation

$$K_v = K_p - T\frac{\partial p}{\partial T}\frac{\partial v}{\partial T}.$$

Let us then make a comparison in the case of ethyl oxide, using E. Wiedemann's value ·3725 for K_p for the vapour at 0°, and Regnault's value ·529 for the liquid at 0° ; then, converting to ergs per degree C., we get

	Vapour at 0°.	Liquid at 0°.
$\frac{\partial}{\partial T}(E-V)$ =	$1{\cdot}68 \times 10^6$	$15{\cdot}3 \times 10^6$,
K_v or $\frac{\partial}{\partial T}(E-P)$ =	$14{\cdot}4 \times 10^6$	$17{\cdot}9 \times 10^6$.

Thus we see that while in the liquid $\partial(E-V)/\partial T$ is nearly equal to $\partial(E-P)/\partial T$, there is a great difference in the vapour :
$\partial(V-P)/\partial T = 12{\cdot}7$ for the vapour and only 2·6 for the liquid. Or, while K_v is nearly the same in the two states, $\partial(E-V)/\partial T$ has in the liquid state increased to nine times its value in the vaporous. We have here, therefore, an interesting opening into the regions of chemic force ; but meanwhile we must restrict ourselves to the question of molecular force at present in hand, calling attention, however, to the fact that our energy term in its two forms for elements and its two forms for compounds is well worthy of the closest study. It summarizes a lot of information about the internal dynamics of molecules—perhaps about the relations of matter and æther ; but these would need to be extracted by a special research on the term and its relation to our experimental knowledge of specific heat. It is worth mentioning here that Clausius's equation of the virial, as usually applied to molecular physics, takes no account of the mutual action of matter and æther—an action which we know must exist, from the radiation of heat by gases as well as by liquids and solids. According to ordinary views of the æther this may be neglected, on account of the smallness of the mass and of the specific heat of the æther ; but it is well to remember that we are neglecting it.

6. *Consideration of Van der Waals's generalization.*—We are now in a position to consider how far Van der Waals's generalization holds, namely :—If the volume, pressure, and temperature are measured for each substance in terms of the critical values as units, then one and the same aw holds for all substances.

In the first place, we see from what has gone before that the same law cannot apply to both elements and compounds, nor can the alcohols and water follow the same law as regular compounds.

In the case of the elements and methane we have the critical volume, pressure, and temperature given in terms of R, l, and k by three relations (see end of Section 2),

$$v_c = 3k/2, \quad p_c = \frac{4}{27}\frac{l}{k^2}, \quad T_c = \frac{16}{27}\frac{l}{Rk}.$$

Whence, in the supracritical equation replacing R, l, and k by their values in terms of v_c, p_c, T_c, we get

$$\frac{pv}{p_c v_c} = \frac{8}{3}\frac{T}{T_c}\left(1 + \frac{1}{\frac{3v}{v_c} - 1}\right) - \frac{3v_c}{v};$$

which shows that when the critical values are made the units in the measurements of the variables, one and the same law holds for the elements above the critical volume.

Below the critical volume we have

$$\frac{pv}{p_c v_c} = \frac{9}{16}\frac{T}{T_c}\left(1 + b\frac{1 - \frac{v}{v_c}}{\frac{v}{v_c} - \frac{\beta}{v_c}}\right) - \frac{3v_c}{v}.$$

We have seen that b is nearly the same for these bodies and that β/v_c is approximately constant, so that below the critical volume the elements and methane all follow approximately the same law.

In the case of compounds, we have (see Section 4, at the beginning)

$$v_c = 7k/6, \quad p_c = \frac{36}{409}\frac{l}{k^2}, \quad T_c = \frac{120}{409}\frac{l}{Rk},$$

with which, eliminating R, k, and l from the supracritical equation, we get

$$\frac{pv}{p_c v_c} = \frac{20}{7}\frac{T}{T_c}\left(1 + \frac{2}{\frac{7}{6}\frac{v}{v_c} + 1}\right) - \frac{409}{42}\frac{1}{\frac{7}{6}\frac{v}{v_c} + 1}.$$

Hence, above the critical volume the compounds follow the same law among themselves.

In the same way, below the critical volume we get for compounds:—

$$\frac{pv}{p_c v_c} = \frac{20}{7} \cdot \frac{25}{13} \frac{T}{T_c} \left(1 + \frac{\sqrt{T}}{B} \cdot \frac{1 - \frac{v}{v_c}}{\frac{v}{v_c} - \frac{\beta}{v_c}} \right) - \frac{409}{98} \frac{v_c}{v}.$$

One and the same law holds for compounds below the critical volume only if B varies as the square root of the critical temperature, and if β is proportional to the critical volume : in the elements we have found the latter condition to hold approximately, and so we are prepared to find it do so for compounds. The following Table compares B with $\sqrt{T_c}$ and β with k, which is $6v_c/7$ for the five compounds for which we have as yet found k. The values of B and β for NH_3 and N_2O were obtained from Andréeff's data for the expansion of these bodies as liquids (*Ann. Chem. Pharm.* cx.) and for SO_2 from Jouk's (Wied. *Beibl.* vi.).

TABLE XXI.

	k.	β.	k/β.	B.	$B/\sqrt{T_c}$.
$(C_2H_5)_2O$	4·066	1·11	3·7	63	2·9
CO_2	1·76	·69	4·0	54	3·0
SO_2	2·08	·55	3·8	71	3·6
NH_3	4·8	1·22	3·9	70	3·6
N_2O	2·3	·66	3·5	55	3·1

In these bodies we find a fair approximation to proportionality between β and k on the one hand, and between B and $\sqrt{T_c}$ on the other ; to the same degree of approximation Van der Waals's generalization can be applied to compounds below the critical volume (excluding of course such exceptional bodies as the alcohols and water).

The accurate statement of the generalization ought then to be as follows :—When the variables are expressed in terms of their critical values as units, then down to the critical point compound bodies with certain exceptions have all one and the same characteristic equation, but below the critical point they have closely similar but not identical equations.

It is a remarkable fact that Van der Waals should have been led to his valuable generalization by means of a form of equation which completely fails to apply to the substances which are the subject of the generalization. As a point in the history of this branch of molecular physics, it calls for mention that Waterston, in the Phil. Mag. vol. xxxv. (1868), had prac-

tically discovered the generalization, and expressed it in its most striking aspects by means of several diagrams for a number of bodies; but the verbal expression of his results was so unsystematic, and withal so crabbed, that his work has been overlooked.

There is one typical application of the generalization which is of special importance—to the relation between pressure and temperature of saturation. If with the aid of our equations we trace the complete isothermals for temperatures below the critical, we shall get curves with the James Thomson double-bend as shown in Ramsay and Young's isothermals for ether (Phil. Mag. May 1887).

According to Maxwell's thermodynamical deduction, the pressure of saturation at a given temperature is that corresponding to the line of constant pressure which cuts off equal areas in the two bends, a result which Ramsay and Young verified by actual measurement on their curves.

Let v_3 and v_1 be the volumes of saturated vapour and liquid at pressure P and temperature T; then Maxwell's principle gives us that the pressure of saturation is defined by the three equations:—

$$\mathrm{P}(v_3-v_1)=\int_{v_1}^{v} p\,dv,$$

$$\mathrm{P}v_3=\mathrm{RT}\left(1+\frac{2k}{v_3+k}\right)-\frac{l}{v_3+k},$$

$$\mathrm{P}v_1=\tfrac{25}{13}\mathrm{RT}\left(1+\frac{\sqrt{\mathrm{T}}}{\mathrm{B}}\,\frac{\frac{7}{6}k-v_1}{v_1-\beta}\right)-\frac{l}{2v_1}.$$

v_3 is given in terms of P and T by a quadratic, and can therefore be eliminated from the integral when evaluated; v_1 is given by a cubic, but as $\mathrm{P}v_1$ can for practical purposes be put 0, a very close approximation to v_1 can be obtained also from a quadratic. The resulting relation between P and T, which is the law of saturation, involves the constants R, k, l, B, and β.

The actual evaluation of the integral would of course proceed in three stages, corresponding to the supra-, circa-, and infracritical equations. The law of the integral in the first stage from v_3 to $7k/6$, with critical values of the variables as units, would be the same for all compounds; and we have seen that the integral in the other two stages will follow approximately the same law in all cases. Hence if saturation pressures and temperatures are expressed in terms of the critical values, the law of their relation will be approximately the same for all regular compounds.

If this were an absolutely accurate relation, the best means

of testing it would be to take Regnault's formula, with one exponential term,

$$\log p = a + b\alpha^t,$$

and by a simple recalculation from his values for a, b, and α, to cast it in the form

$$\log p/p_c = e + d\gamma^{T/T_c},$$

proving that the constants e, d, and γ are approximately the same for all compounds. But the objection to this plan soon becomes obvious on trial, as the formula owes its empirical convenience to the power of adjustment amongst the constants; and the same difficulty would be experienced with any purely empirical equation.

Accordingly, to test this matter, I have thought it best to compare the pressures of a number of bodies at temperatures which are constant fractions of their critical temperatures, such as $\cdot 6\,T_c$, $\cdot 7\,T_c$, and so on. The ratio of the pressure of any substance to the corresponding pressure of ethyl oxide ought to be approximately the same for that substance at all values of the fraction. Great uncertainty attends the measurement of critical pressures: an error of 20° in the critical temperature is not a large fraction of its value measured from absolute zero, but it makes a large difference in a saturation-pressure, and the critical pressure is the limiting saturation-pressure. In the subjoined Table the critical-pressure ratios are given for what they are worth in the column T_c.

TABLE XXII.

Ratios of Saturation-Pressures at constant fractions of the critical temperature to the Saturation-Pressures of Ethyl Oxide at the same fractions of its critical temperature.

	T_c.	Fractions of T_c.						
		·6.	·65.	·7.	·75.	·8.	·9.	1·0.
Acetone	506	·87	·90	·92	·94	·95	...	1·4
Methyl oxide	404	1·7	1·5	1·4	1·4			
SO_2	428	1·7	1·7	1·7	1·7	1·7	...	2·2
NH_3	404	2·6	2·6	2·5	2·5	2·5	2·4	3·2
H_2S	373	...	3·6	3·2	2·8	2·6	...	2·6
CO_2	305	...	...	...	...	1·8	1·7	2·1
N_2O	308	...	...	...	...	2·4	1·8	2·1
CS_2	548	3·1	2·7	2·3	2·1	...	...	2·1
CCl_4	556	1·3	1·3	1·3	1·2	...	...	1·6
$CHCl_3$	537	1·6	1·5	1·5	1·4	1·3	...	1·6
CH_3Cl	404	1·7	1·5	1·4	1·4	...	...	2·1
C_2H_5Cl	456	1·4	1·4	1·3	1·2	1·2	...	1·5
C_2H_5Br	509	1·9	1·5	1·6	1·5	1·4		
Benzene, C_6H_6	560	1·3	1·3	1·2	1·2	1·1	...	1·4

This table makes it clear enough that, in applying Van der Waals's generalization below the critical volume, we have to do with a first approximation only. The curves for all these diverse bodies excepting CS_2, while not identical, would form a compact bundle about a mean curve from which each body would have its own characteristic departure; and this is just what our study of B and β in Table XXI. should lead us to expect.

7. *Five Methods of finding the Virial Constant.*—The first method is that which we have already exhausted, namely, by means of extended enough observations of the compression and expansion of bodies in the gaseous state.

Second method: to obtain the virial constant l from one measure of the compressibility and of the expansibility at the same temperature of the body as a liquid.

Writing our infracritical equation thus,

$$p = \frac{R'T}{v}\left(1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta}\right) - \frac{l}{2v^2},$$

$$\frac{\partial p}{\partial T} = \frac{R'}{v} + \frac{3}{2}\frac{R'\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} = \frac{3}{2} \cdot \frac{l}{2v^2T} - \frac{R'}{2v} + \frac{3}{2}\frac{p}{T}.$$

But at ordinary low pressures the term p/T is a negligible part of this expression, and we can write

$$\frac{\partial p}{\partial T} = \frac{3}{4} \cdot \frac{l}{v^2T} - \frac{R'}{2v}.$$

Now

$$\frac{\partial p}{\partial T} = -\frac{\partial v}{\partial p}\Big/\frac{\partial v}{\partial p} = -\frac{v_0}{v} \cdot \frac{\frac{1}{v_0}\frac{\partial v}{\partial T}}{\frac{1}{v}\frac{\partial v}{\partial p}} = \frac{v_0}{v} \cdot \frac{a}{\mu},$$

where a and μ are the coefficients of expansion and the compressibility at T as usually defined.

$$\therefore \quad \frac{3}{4}\frac{l}{v^2T} - \frac{R'}{2v} = \frac{v_0}{v}\frac{a}{\mu};$$

$$\therefore \quad l = \frac{4}{3}\left(v_0\frac{a}{\mu} + \tfrac{1}{2}R'\right)vT = \frac{4}{3}\left(v_0\frac{a}{\mu} + \tfrac{25}{26}R\right)vT.$$

In addition to giving us a value of l, this last equation gives a test as to whether the equation applies to a body or not, as the expression on the right-hand side is to be constant at all temperatures if μ is measured at low pressures. But on

account of the experimental difficulties hitherto met with in the measurement of μ, the equation gives no very delicate test, although it might with the improvements in accuracy made within the last few years. In addition to ethyl oxide, the two substances for which we have measurements of both a and μ over the widest range of temperature are ethyl chloride, studied as to expansion by Drion and as to compression by Amagat, who has corrected Drion's coefficients of expansion for change of pressure, and pentane, studied by Amagat and Grimaldi. The following are the values of l calculated from the data at different temperatures for these two substances, with the megadyne taken as unit of force.

Temperature C. ...	0°.	11°.	13°.	20°.	40°.	60°.	80°.	100°.
C_5H_{12} (Grimaldi)...	8530	...	...	7460	7230	8000	8300	9250
C_5H_{12} (Amagat) ...	...	...	9200	...	...	...	...	9250
C_2H_5Cl	...	5820	...	...	...	5450	...	5270

This comparison has been made to show how, from measurements of liquid compressibility at present available, we can get only a fair idea of the value of l, but not an accurate measurement of it.

Amagat has determined the compressibility of several other liquids at different temperatures (*Ann. de Chim. et de Physique*, sér. 5, t. xi.) ; so have Pagliani and Palazzo (Wied. *Beibl.* ix.) and de Heen (Wied. *Beibl.* ix.), but their discussion would bring out nothing more than the above comparison has. De Heen's results would appear to make l diminish with rising temperature in every case ; but he measured his compressibilities in comparison with that of water at the same temperature, and to calculate their values used Pagliani and Vincentini's values for water (Wied. *Beibl.* viii.), which make the compressibility of water much more variable with temperature than Grassi's. If we used Grassi's values in de Heen's experiments, l would remain nearly constant. We will accordingly use the compressibility-method of calculating l subsequently, only to illustrate the general agreement of values derived from purely mechanical experiments with those found by the more accurate methods to which we now proceed. The values found by this second method are tabulated later on in Table XXIV.

Third method of finding the virial constant l: from the latent heat. If we differentiate with respect to T our equation

for saturation-pressures (see Section 6),

$$P(v_3-v_1)=\int_{v_1}^{v_3} p\,dv,$$

we get

$$\frac{dP}{dT}(v_3-v_1)+P\left(\frac{dv_3}{dT}-\frac{dv_1}{dT}\right)=\int_{v_1}^{v_3}\frac{\partial p}{\partial T}dv+P\left(\frac{dv_3}{dT}-\frac{dv_1}{dT}\right);$$

$$\therefore\quad \frac{dP}{dT}(v_3-v_1)=\int_{v_1}^{v_3}\frac{\partial p}{\partial T}dv.$$

Now from thermodynamics we have the relation

$$J\lambda=(v_3-v_1)T\,dP/dT,$$

where λ is the latent heat,

$$\therefore\ J\lambda=\int_{v_1}^{v_3}T\frac{\partial p}{\partial T}dv,$$

which of course could have been written down immediately, for if we write it in the form

$$J\lambda=\int_{v_1}^{v_3}\left(T\frac{\partial p}{\partial T}-p\right)dv+Pv_3-Pv_1,$$

we remind ourselves that the latent heat of evaporation of a liquid is the heat supplied to neutralize a Thomson and Joule cooling effect.

We must evaluate the integral in three stages,

$$\int_{v_1}^{v_3}T\frac{\partial p}{\partial T}dv=\int_{k'}^{v_3}T\frac{\partial p}{\partial T}dv+\int_{k}^{k'}T\frac{\partial p}{\partial T}dv+\int_{v_1}^{k}T\frac{\partial p}{\partial T}dv,$$

using in each integral the equation that holds between its limits.

In the first,

$$pv=RT\left(1+\frac{2k}{v+k}\right)-\frac{l}{v+k},$$

$$\frac{\partial p}{\partial T}=\frac{R}{v}\left(1+\frac{2k}{v+k}\right),$$

$$T\frac{\partial p}{\partial T}=p+\frac{l}{v+k}.$$

In the second,

$$pv=R'T\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)-\frac{l}{v+k},$$

$$T\frac{\partial p}{\partial T}=\frac{3}{2}\left(p+\frac{l}{v(v+k)}\right)-\frac{R'T}{2v}.$$

In the third,

$$pv = \mathrm{R'T}\left(1 + \frac{\sqrt{\mathrm{T}}}{\mathrm{B}} \cdot \frac{k'-v}{v-\beta}\right) - \frac{l}{2v^2},$$

$$\mathrm{T}\frac{\partial p}{\partial \mathrm{T}} = \frac{3}{2}\left(p + \frac{l}{2v^2}\right) - \frac{\mathrm{R'T}}{2v}.$$

Hence

$$\mathrm{J}\lambda = \int_{k'}^{v_3}\left(p + \frac{l}{v+k}\right)dv + \int_{k}^{k'}\left\{\frac{3}{2}\left(p + \frac{l}{v+k}\right) + \frac{\mathrm{R'T}}{2v}\right\}dv$$
$$+ \int_{v_1}^{k}\left\{\frac{3}{2}\left(p + \frac{l}{2v^2}\right) - \frac{\mathrm{R'T}}{2v}\right\}dv$$
$$= \int_{v_1}^{v_3} pdv + \frac{1}{2}\int_{v_1}^{k'} pdv + \int_{k}^{v_3}\frac{ldv}{v(v+k)} + \frac{1}{2}\int_{k}^{k'}\frac{ldv}{v(v+k)}$$
$$+ \frac{3}{4}\int_{v_1}^{k}\frac{ldv}{v^2} - \frac{1}{2}\int_{v_1}^{k'}\frac{\mathrm{R'T}dv}{v}$$
$$= \mathrm{P}(v_3 - v_1) + \frac{1}{2}\int_{v_1}^{k'} pdv + \frac{l}{k}\log\frac{2v_3}{v_3+k} + \frac{l}{2k}\log\frac{2k'}{k'+k}$$
$$+ \frac{3l}{4}\left(\frac{1}{v_1} - \frac{1}{k}\right) - \frac{\mathrm{R'T}}{2}\log\frac{k'}{v_1}.$$

We must now evaluate the only integral that has been left unevaluated,

$$\int_{v_1}^{k'} pdv = \int_{v_1}^{k'}\frac{\mathrm{R'T}}{v}\left(1 + \frac{\sqrt{\mathrm{T}}}{\mathrm{B}} \cdot \frac{k'-v}{v-\beta}\right)dv - \int_{k}^{k'}\frac{ldv}{v(v+k)} - \int_{v_1}^{k}\frac{ldv}{2v^2}$$
$$= \mathrm{R'T}\log\frac{k'}{v_1} + \frac{\mathrm{R'T}\sqrt{\mathrm{T}}}{\mathrm{B}}\left(\frac{k'-\beta}{\beta}\log\frac{k'-\beta}{v_1-\beta} - \frac{k'}{\beta}\log\frac{k'}{v_1}\right)$$
$$- \frac{l}{k}\log\frac{2k'}{k'+k} - \frac{l}{2}\left(\frac{1}{v_1} - \frac{1}{k}\right).$$

These last expressions are the only ones that introduce B and β into the value of $\mathrm{J}\lambda$, and it is desirable to remove these two constants. At low pressures we can neglect the pv term in the infracritical equation, and we get

$$\frac{\mathrm{R'T}\sqrt{\mathrm{T}}}{\mathrm{B}} = \left(\frac{l}{2v_1} - \mathrm{R'T}\right)\frac{v_1-\beta}{k'-v_1};$$

removing B by means of this we get

$$\mathrm{J}\lambda = \mathrm{P}(v_3 - v_1) + \frac{l}{k}\log\frac{2v_3}{v_3+k} + \frac{l}{2}\left(\frac{1}{v_1} - \frac{1}{k}\right)$$
$$+ \frac{1}{2}\left(\frac{l}{2v_1} - \mathrm{R'T}\right)\frac{v_1-\beta}{k'-v_1}\left(\frac{k'-\beta}{\beta}\log\frac{k'-\beta}{v_1-\beta} - \frac{k'}{\beta}\log\frac{k'}{v_1}\right).$$

We can now remove β and greatly simplify this equation, if we apply it to latent heats near the ordinary boiling-point T_b. The last term taken in its entirety has a small numerical value compared to the rest, so that in it we can make approximations without any sacrifice of accuracy worth considering: we have seen that β is approximately proportional to k (see Table XXI.) and v_1, the volume of the liquid at the boiling-point, may be assumed to be approximately proportional to k' the volume at the critical temperature, and $k'=7k/6$: hence the coefficient of $(l/2v_1-R'T)$ in the last term is approximately the same for all bodies and we can evaluate it for ethyl oxide; call it C. Again, in $P(v_3-v_1)$ neglect v_1 and assume the gaseous law $Pv_3=RT_b$. And further, k is small compared to v_3, so that $2v_3/(v_3+k)$ is nearly 2, and its value for ethyl oxide can be applied to all bodies. $R'=25R/13$. Hence multiplying by M the molecular weight we can write

$$\frac{Ml}{k}\left\{\frac{1}{2}\left(\frac{k}{v_1}-1\right)+\log\frac{2v_3}{v_3+k}+\frac{C}{2}\frac{k}{v_1}\right\}=JM\lambda+MR\left(\frac{25}{13}C-1\right)T_b.$$

MR is the same for all bodies, and T_b is the absolute boiling-point. This equation still involves k as well as l; when k is not known we must eliminate it by means of our previous assumption, namely, that k is proportional to v_1, which we know to be approximately true; in so far as it is inexact it will introduce inexactness into our calculation of l. Accordingly in symbols $k/v_1=r$, where r is the same for all bodies, and can be found for ethyl oxide. Making the numerical reductions we get

$$Ml/v_1=66{\cdot}5\,M\lambda-101T_b$$

as the equation which gives l in terms of the megadyne as unit of force, when λ is the latent heat of a gramme in calories and v_1 its volume in cubic centimetres at the absolute boiling-point T_b. This equation will be abundantly verified afterwards in Table XXIV.; but meanwhile, if to test it we apply it to calculate the latent heat of ethyl oxide, we find $\lambda=83{\cdot}4$, whereas several experimenters have agreed in an estimate of about 90; but, on the other hand, Ramsay and Young (Phil. Trans. 1887) have made a special study of the terms in the thermodynamic relation $J\lambda=(v_3-v_1)TdP/dT$, and have so calculated values of λ almost up to the critical temperatures, their value at the boiling-point is 84·4, and there is the same amount of discrepancy between their values at higher temperatures and Regnault's experimental determinations. Yet Perot, who has made an elaborate study (*Ann. de Ch. et de Ph.* sér. 6, t. xiii.) both of λ experimentally

and of the quantities involved in its calculation by the thermodynamic relation, has found the most perfect harmony between the results of the two methods. Now at 30° C. Perot gives as the saturation-volume of the vapour 400·4, and the saturation-pressure ·635 metre, while Ramsay and Young's values are 374 and ·648 metre; but if ethyl oxide were a perfect gas, under Perot's pressure of ·635 metre it would have a volume of 400·8, almost identical with his value: yet we cannot imagine that ethyl oxide under this pressure and at this temperature is so nearly a perfect gas as this would imply, unless there is some remarkable discontinuity in its behaviour at high volumes. Accordingly, in spite of the thoroughness of the researches of both Perot and Ramsay and Young, we are on the horns of a triple dilemma, from which only some experimental repetition can deliver us, and demonstrate where the cause of these discrepancies lies. Wüllner and Grotrian (Wied. *Ann.* xi.) have put on record the results of experiments which indicate the cause; they find the pressure of condensation measurably different from the ordinarily measured saturation-pressure,—a fact explaining the difficulty of measuring v_3 accurately, and showing also that the values of dP/dT are not so reliable as usually supposed.

Our last equation is verified by, and shows us the cause of, an interesting relation that has been independently discovered and expressed in different forms, between the molecular latent heat and the boiling-point, by Pictet (*Ann. de Ch. et de Ph.* sér. 5, t. ix. 1876), Trouton (Phil. Mag. xviii. 1884), and Ramsay and Young (Phil. Mag. xx. 1885), namely, that the molecular latent heats of fluids are nearly proportional to their absolute boiling-points. Now we have seen that $T_c = 120l/409Rk$ (Section 4), and I have noticed that a large number of substances have their ordinary absolute boiling-points nearly equal to $2T_c/3$, and k is nearly proportional to v_1, say is equal to $2{\cdot}8\,v_1$, as it is for ethyl oxide. Hence we have

$$\frac{3}{2}T = \frac{120l}{409\,R\,2{\cdot}8\,v_1};$$

$$\therefore\ Ml = 14{\cdot}3\,MRv_1T_b = 1190v_1T_b,$$

when the megadyne is the unit of force; hence from our equation for Ml in terms of λ we have

$$1190T_b = 66{\cdot}5\,M\lambda - 101\,T_b;$$

$$\therefore\ 1291\,T_b = 66{\cdot}5\,M\lambda \quad \text{or} \quad M\lambda = 19{\cdot}4T_b,$$

or the molecular latent heat is proportional to the absolute boiling-point.

(It is to be noted that $Ml = 1190\, v_1 T_b$ gives a rough means of obtaining l from the boiling-points and the volumes at the boiling-points of liquids, which might be convenient when better data are wanting.)

Robert Schiff (*Ann. der Chem.* ccxxxiv.) has made the most accurate determinations to test this relation between molecular latent heat and boiling-point. For 29 compounds of the form $C_nH_{2n}O_2$, from ethyl formiate up to isoamyl valerate, he finds $M\lambda = 20{\cdot}8T_b$ in the mean, the greatest departures being 20·4 for propyl isobutyrate, and 21·1 for propyl formiate; for 8 hydrocarbons of the benzene series he finds a mean coefficient 20 with 19·8 for cymene and 20·6 for benzene as the greatest departures. To these 37 examples we will add the following from Trouton's paper, doubling his numbers, as he used density instead of M.

TABLE XXIII.—Values of $M\lambda/T_b$.

C_2H_5Cl.	$CHCl_3$.	CCl_4.	$AsCl_3$.	$SnCl_4$.	SO_2.	CS_2.
21	22	21	21	20	23	21

$(C_2H_5)_2O$.	$(C_5H_{11})_2O$.	$(CH_3)_2CO$.	$C_{10}H_{16}$.	$(C_2H_5)_2C_2O_4$.
22	24	23	22	23

The mean value of the coefficient is higher than that deduced theoretically above (19·4), because in round fraction we wrote $T_b = 2T_c/3$, but the general truth of the relation is well enough brought out.

Fourth method of finding the virial constant l: from the critical temperature and pressure. Now we have (Section 4),

$$T_c = 120\, l/409Rk, \quad p_c = 36l/409\, k^2,$$

$$\therefore\ T_c/p_c = 10k/3R \quad \text{and} \quad l = 409R^2T_c^2/400\, p_c,$$

this is for compounds; for elements $l = 27R^2T_c^2/64p_c$. Where both the critical pressure and temperature are known, this gives l theoretically with accuracy, but practically the difficulties in measuring the critical pressure introduce inaccuracy. In the relation $T_c/p_c = 10k/3R$, as R varies inversely as the molecular weight, we see that the molecular domains (Molecular volumes) of bodies at the critical temperature are

proportional to the quotient of critical temperature by critical pressure, a relation which Dewar has proved experimentally (Phil. Mag. xviii. 1884) for 21 volatile bodies, for which he has determined and collected the data. These with other data since published enable us to determine values of l for certain bodies for which the other methods are not available.

As there are many more critical temperatures determined up to the present than critical pressures, and as we have seen that an error in the critical temperature is of less relative importance than an error in the critical pressure, we can make ourselves independent of critical pressures with advantage, by employing the approximation that has already been useful to us, that k is proportional to the volume of the liquid at the boiling-point or $k=2{\cdot}83v_1$. Then

$$\mathrm{M}l=409\mathrm{MRT}_c k/120=800\mathrm{T}_c v_1$$

approximately, with the megadyne as unit of force. This is a more accurate form of the relation $\mathrm{M}l=1190\mathrm{T}_b v_1$ given above, in which we assumed the approximation $\mathrm{T}_b=2\mathrm{T}_c/3$.

8. *Fifth or Capillary Method of finding the Internal Virial Constant*, with digressions on the Brownian movement in liquids and on molecular distances.—So far we have been proceeding on a purely inductive path, with two deductive guides in Clausius's equation of the virial and in the law of the inverse fourth power, which requires that the internal virial should vary inversely as the volume. But now, in passing on to our fifth and most useful method of finding l from surface-tension, we must employ a deductive relation between l and surface-tension, furnished by the law of the inverse fourth power. In a previous paper (Phil. Mag. July 1887) it was shown that if the law of force between two molecules of mass m, at distance r apart is $3\mathrm{A}m^2/r^4$, then the internal virial for the molecules in unit mass is $3\pi\mathrm{A}\rho \log \mathrm{L}/a$, ρ being density, and L a finite length of the order of magnitude of the linear dimensions of the vessels used in physical measurements, a being the mean distance apart of the molecules. The ratio L/a remains the same for a given mass whatever volume it occupies, but I also assumed that L/a is so large a number that $\log \mathrm{L}/a$ would hardly be affected by such large variations as might occur in the value of L when the behaviour of a kilogramme of a substance was compared with that of a milligramme. To remove the haziness of this assumption, I will now make a more accurate evaluation of the internal virial.

By definition it is $\frac{1}{2}\,.\,\frac{1}{2}\,.\,\Sigma\Sigma 3\mathrm{A}m^2/r^3$, and we will evaluate it

for a spherical mass. To cast it into the form of an integral, take any molecule m amongst the number n in a spherical vessel of radius R; gather it to its centre as a true particle and spread the remaining $n-1$ in a uniform continuous mass separated from m by a small spherical vacuum of radius a, so chosen that the virial of m and the continuous mass is the same as that of m and the $n-1$ molecules.

Suppose m at the point O, and the centre of the vessel at C, and let $OC=c$. Take OC as axis of x and any two rectangular axes through O as axes of y and z. Let polar coordinates $r\,\theta\,\phi$ be related to these in the usual manner. Then the equation to the surface of the sphere is

$$(x-c)^2+y^2+z^2=R^2 \quad \text{or} \quad r^2-2cr\sin\theta\cos\phi+c^2-R^2=0.$$

Let r_1 and r_2 be the two roots of this equation in r so that $r_1r_2=R^2-c^2$. Then m^2/r^3 can be replaced by

$$m\rho r^2\sin\theta\,d\theta\,d\phi\,dr/r^3,$$

and

$$\Sigma m^2/r^3 \text{ by } \iiint m\rho\sin\theta\,d\theta\,d\phi\,dr/r.$$

If we integrate with respect to r on one side of the plane yz from a to r_1 and on the other from a to r_2 and add the two results, then we have to take θ and ϕ each between 0 and π, thus:

$$\Sigma m^2/r^3=\int_0^\pi\int_0^\pi m\rho\sin\theta d\theta\,d\phi\left[\int_a^{r_1}dr/r+\int_a^{r_2}dr/r\right].$$

The two integrals in brackets give

$$\log r_1r_2/a^2=\log(R^2-c^2)/a^2.$$

Hence

$$\Sigma m^2/r^3=2\pi m\rho\log(R^2+c^2)/a^2.$$

To perform the second summation we can first add the values of the last expression for all the molecules at distance c from the centre of the vessel, and write the result in the form

$$2\pi\rho 4\pi\rho c^2dc\log(R^2-c^2)/a^2,$$

and we then have

$$\tfrac{1}{2}\cdot\tfrac{1}{2}\Sigma\Sigma 3Am^2/r^3=6A\pi^2\rho^2\int_0^{R-a}c^2dc\log(R^2-c^2)/a^2.$$

Evaluating the integral, this becomes

$$6A\pi^2\rho^2\left\{\frac{1}{3}(R-a)^3\log\frac{2R-a}{a}-\frac{2}{9}(R-a)^3-\frac{2}{3}R^2(R-a)+\frac{R^3}{3}\log\frac{2R+a}{a}\right\},$$

in which, neglecting unity in comparison with the large number R/a, we get

$$A\pi^2\rho^2R^3\{4\log 2R/a-16/3\}.$$

But if W is the total mass in the vessel, then

$$W = 4\pi r^3 \rho/3,$$

and we get

$$W a\pi\rho\{3 \log 2R/a - 4\}.$$

When $W = 1$ the first term of this becomes identical with the value of the internal virial previously given, with 2R written instead of L. Replacing R by its value in terms of W and ρ, we get for the internal virial of mass W,

$$WA\pi\rho(\log 6W/\pi\rho a^3 - 4).$$

As ρa^3 is constant, we see that for a given mass the internal virial for molecular force varying inversely as the fourth power is rigorously proportional to the density, but it is not purely proportional to the mass. Although the number $6W/\pi\rho a^3$ is a large one, and has a logarithm varying slowly with W, yet large enough variations in W can affect it appreciably, as we see if provisionally we accept Sir W. Thomson's estimate of 2×10^{-9} centim. as the lowest possible value for a. Suppose $\pi\rho = 3$, then $6W/\pi\rho a^3$ is $10^{27}W/4$, and if W is 4000, 4, or ·004 grm., then the values of $\log 6W/\pi\rho a^3$ are as 30, 27, and 24, and we have a larger mass variation of the internal virial than is likely to have escaped detection in its effects, such as a difference in the density, expansion, compressibility, latent heat, and saturation-pressures of a liquid as measured on a milligramme, from their values as measured on a kilogramme. The raising of this difficulty suggests to us in passing that there exists a department of microphysics in which little has as yet been done by the experimenter, and that great interest would attach to a research determining when a mass variation of the properties usually spoken of as physical constants actually sets in.

But meanwhile we must scrutinize more closely the meaning of our last result. According to the views of Laplace (and of the early elasticians), if a plane be drawn dividing a mass of solid or liquid into two parts, then, in consequence of molecular force, the one part exercises a resultant attraction on the other, and this has to be statically equilibrated by a pressure (called the molecular or internal pressure) acting across the plane, a conception which is necessary in any purely statical theory of elasticity. Adopting for the moment this mode of viewing things, we see that our result amounts to this, that the internal pressure is measurably greater at the centre of a kilogramme than of a milligramme.

But if we try to carry out the kinetic theory in its integrity,

we must reject the idea of a statical pressure, and replace it by its kinetic equivalent of a to and fro transfer of momentum; this may take place as a quite indiscriminate traffic of individual molecules across the plane, or as such a traffic modified by the existence of streams of molecules in opposite directions. If streams, or motions of molecules in swarms, actually exist in fluids, then our interpretation of the equation of the virial would have to take account of their existence. The kinetic energy of the motion of a swarm as a whole would not count as heat but as mechanical energy, and for the amount of it we should have approximately the kinetic energy of the swarm motion equal to the virial of the forces between the swarms. Therefore we require to divide the energy into two parts, that of molecular motion inside the swarm constituting heat and that of the swarm; in the same way the internal virial is divided into two parts, one within each swarm, the other between the swarms. But the swarms could on the average be regarded as equivalent to spheres of radius L, where L must be supposed nearly independent of mass and liable to the same variations with temperature and pressure as the linear dimensions of any quantity of the liquid, so that L is proportional to a, and our expression (theoretical) $WA\pi\rho(3 \log 2L/a-4)$ for the internal virial becomes purely proportional to the mass and purely proportional to the density, as $3Wl/4v$ our experimental internal virial for a mass W of a compound liquid is.

This hypothesis would affect somewhat the rigorousness of certain thermodynamical relations as usually interpreted, such as $J\lambda=(v_3-v_1)T dp/dT$, since it provides a supply of internal mechanical energy not taken account of; but if this supply is only slightly variable with pressure and temperature it would make little difference in most parts of thermodynamics.

With the addition of this hypothesis of molecular swarms, which will be used only in calculating molecular distances, and will not affect at all the rest of our work, the law of the inverse fourth power is brought into strict harmony with the behaviour of compound liquids and of elements both as liquids and gases. We must therefore inquire what experimental evidence there is for the existence in liquids of a motion of swarms of molecules, possessing the remarkable property of not being degraded to heat as ordinary visible motions are. In the motion long familiar to microscopists as the Brownian movement we have such evidence. Gouy has recently (*Compt. Rend.* cix. p. 103) recalled the attention of physicists to this remarkable ceaseless motion of granules in liquids. He states that it occurs with all sorts of granules, and with an

intensity less as the liquid is more viscous and as the granules are larger. It occurs when every precaution is taken to ensure constant temperature, and to ensure the absence of all external causes of motion. Granules of the same size but as different in character as solid granules, liquid globules, and gaseous bubbles, show but little difference in their motions—a fact which proves that the cause is to be looked for not in the granules themselves but in the liquid, the granules being merely an index of motions existing in the liquid. The most pronounced character of the motion is its rapid increase with diminishing size of granules, so that all that is seen under the microscope is the limit of movements of unknown magnitude. Gouy considers the Brownian movements to be a remote result of the motion of the molecules themselves, but according to what we know of molecular dimensions I fancy that the Brownian movement must be considered rather as a sign of the motion of swarms of molecules. If swarms of molecules are weaving in and out amongst one another, so that the average transfer of momentum at a point is the same in all directions, then the vibratory agitation of granules amongst the swarms is just what we should expect. The striking fact about the Brownian movement is that it is ceaseless; it is never degraded into heat. This alone forces us to conceive a form of motion existing in liquids on a larger scale than molecular motion but possessing its character of permanence; in other words, the motion of swarms of molecules.

The existence of swarms would not affect our views of the rise of liquids in capillary tubes as a purely statical question; so that, for the connexion between molecular force and surface-tension, we can use the calculation given in another paper (Phil. Mag. April 1889) (rather badly affected with misprints), where I have shown that the surface-tension of liquids that wet glass, measured in tubes so narrow that the meniscus-surface is a hemisphere, is given by the equation

$$\alpha = \pi\bar{\rho}^2 \mathrm{A} e/(2+\sqrt{2})\,;$$

where $\bar{\rho}$ is the average density of the capillary surface-film (to be written also $1/\bar{v}$), and e is the distance which we must suppose to be left between a continuous meniscus and the base of a continuous column raised by its attraction, if the action between the continuous distributions is to be the same as in the natural case of discontinuous molecular constitution of meniscus and column. The distance e is not identical with the length a which occurs in our theoretical value of the internal virial of unit mass,

$$\mathrm{A}\pi\rho(3\log 2\mathrm{L}/a - 4) = \frac{3}{2}\frac{l}{2v},$$

but it is closely proportional to it. If we can find the relation between e and a, then from capillary determinations we can obtain relative values of the virial constant l which, as we have already found some absolute values of l, can be converted to absolute values; at the same time, too, we shall be able to find a value of a the mean distance apart of the molecules.

To find the relations between e and a we can proceed thus. If we have a single infinite straight row of molecules at a distance a apart, the force exerted by one half of it on the other is

$$\Sigma_{n=0}^{n=\infty}\,\Sigma_{p=1}^{p=\infty}\frac{3\mathrm{A}m^2}{(p+n)^4a^4},$$

which can easily be evaluated as approximately $3{\cdot}6\mathrm{A}m^2/a^4$. Two infinite continuous lines in the same line, of density m/a with distance e between their contiguous ends, would exert a force

$$\frac{3\mathrm{A}m^2}{a^2}\int_e^\infty\int_0^\infty\frac{dx\,dy}{(x+y)^4}$$

on one another; this is equal to $\mathrm{A}m^2/2a^2e^2$. If, then, the continuous distribution is to be equal to the molecular, we nave

$$e^2=a^2/7{\cdot}2,\quad e=a/2{\cdot}7.$$

Again, if along two infinite axes one at right angles to the other and terminating in an origin O at its middle point molecules are arranged along each at distance a apart starting from O, then the force exerted by the unlimited row on the other is

$$2\Sigma_{p=1}^{p=\infty}\,\Sigma_{n=1}^{n=\infty}\frac{3\mathrm{A}m^2n}{(p^2+n^2)^{\frac{5}{2}}a^4}+\Sigma_{p=1}^{p=\infty}\frac{3\mathrm{A}m^2}{p^4a^4},$$

which can be evaluated at about $5\mathrm{A}m^2/a^4$.

Replace the rows by two continuous line-distributions of density m/a, the one terminating at a distance e from O: it is required to find e so that the force may be the same as this. The force is

$$\frac{6\mathrm{A}m^2}{a^2}\int_e^\infty\int_0^\infty\frac{y\,dy\,dx}{(x^2+y^2)^{\frac{5}{2}}}=\mathrm{A}m^2/a^2e^2.$$

Hence in this case

$$e^2=a^2/5,\quad e=a/2{\cdot}2.$$

From these two simple cases we get an idea of the relation between e and a. The case of a meniscus attracting the column which it raises in a capillary tube is more analogous to the second than to the first, and it is easy to see that in the

case of the meniscus we can say that e is not less than $a/2{\cdot}2$. It will suffice to write $e=a/2{\cdot}2$.

Now according to the definition of a in our theoretical expression for the internal virial, it is the radius of the spherical vacuum artificially used to represent the domain of a molecule; but as it occurs in the expression $\log 2\mathrm{L}/a$, where $2\mathrm{L}/a$ is a very large number and the value of L is indefinite, we see that there is no inaccuracy in making it identical with a the mean distance apart of the molecules. However, for the sake of formal completeness, we can easily find the relation between the two quantities which we have denoted by the one symbol a. Let us now denote by x the mean distance apart of the molecules, that is the edge of the cube in a cubical distribution of the molecules; then, from the definition of a, x and a are connected by the relation

$$\Sigma \mathrm{A}m^2/r^3=\int_a^{\mathrm{R}} 4\pi \mathrm{A}m^2 dr/x^3 r,$$

the summation being extended to all the molecules in a sphere of radius R. By actual summation up to $\mathrm{R}=5x$ we find approximately $a={\cdot}9x$.

With our previous estimate of e as $a/2{\cdot}2$, which we must now write $x/2{\cdot}2$ on account of our change of symbol for mean distance apart, we have the two equations,

$$l=\mathrm{A}\pi(4\log 2\mathrm{L}/{\cdot}9x-16/3),$$

$$\alpha=\pi\bar{\rho}^2\mathrm{A}x/2{\cdot}2(2+\sqrt{2}).$$

We can replace $\bar{\rho}$ by ρ, the difference between them being necessarily very slight. Then for ethyl oxide we have the following data: α at the boiling-point according to Schiff is $1{\cdot}57$ grammes weight per metre, or $1{\cdot}57/10^5$ kilog. per cm.; l is 7500 kilog. cm.^{4}, and $v_1=1{\cdot}44$ cm.^{3} Eliminating A from the two equations, we have a relation between x and L, namely

$$x=7{\cdot}5v_1^2\frac{\alpha}{l}(9{\cdot}2\log_{10}2\mathrm{L}/{\cdot}9x-16/3).$$

L being hypothetical is not known to us, but we can give it a series of possible values, and calculate by trial from the last equation the corresponding series of values for x, with the following results:—

L.	x.
$1/10^5$ cm.	$4{\cdot}6/10^7$ cm.
$1/10^4$,,	$7{\cdot}7$,, ,,
$1/10^3$,,	$11{\cdot}0$,, ,,

As it is subsequently to be shown that in liquid ethyl oxide and in all regular compound liquids the molecules are paired, and that each pair acts on the others as if it were a single molecule, we may estimate it as likely that the mean distance apart of the pairs in ethyl oxide is between 1 and 10 micromillimetres ($1/10^6$ mm.). This result, though 100 times as large as Sir William Thomson's limits for the distance apart of molecules in liquids, namely 2×10^{-9} cm. and 7×10^{-9} cm., is yet in better agreement with the estimate of molecular distances arrived at by Rücker (Journ. Chem. Soc. 1888) as the most probable result obtainable from the most important attempts yet made to measure the range of molecular forces. The most suggestive of these is Reinold and Rücker's discovery, that the equilibrium of a soap-solution film becomes unstable when its thickness is reduced to between 96 and 45 micromillimetres, but again becomes stable when the thickness is still further reduced to 12 micromillimetres. At the latter thickness the film shows black in reflected light. If the intermolecular distances are nearly the same in soap-solutions as in liquid ethyl oxide, then the black film must be regarded as consisting of a single layer of molecules or groups of molecules (in the case of water the molecules will subsequently be shown to go in double pairs). This is an intelligible result, and gives the simplest explanation of Reinold and Rücker's beautiful discovery of a stable thickness supervening on the unstable, for we recognize a single layer of molecules as a stable configuration. Of course it is to be understood that what we mean by the thickness of a single layer of molecules is the one nth part of the thickness of n layers; and if the black film is really only a single layer, it is in this sense that Reinold and Rücker's estimate of 12 micromms. is to be taken, for they did not measure an actual distance from the front to the back of a black film, but only estimated from accurate and accordant measurements, made in entirely different manners, that the number of layers in the black film is to the number in a thickness of 1 centim. as 12 micromms. is to 1 centim.

If the black film consists really of only a single layer of molecules, it is surely a hopeful sign for molecular physics that measurements should have been possible on it, though only visible through its invisibility.

If, encouraged by this experimental support, we say that in round numbers the mean distance between the pairs of molecules in liquid ethyl oxide is 10 micromms., then one gramme contains $2v_1 \times 10^{18}$ molecules, or the mass of a single molecule is

$$1/2{\cdot}88 \times 10^{18} \text{ grm.} = 3{\cdot}5/10^{19},$$

and so the mass of an atom of H is

$$3{\cdot}5/74 \times 10^{19} = 5/10^{21} \text{ grm. nearly.}$$

It would lead us too far from our present purpose to discuss other estimates of molecular distance, especially as Reinold and Rücker's measurement of the black film is the most definite and striking yet made of these minute distances; but the question of the range of molecular force is of special importance to us.

Quincke (Pogg. *Ann.* cxxxvii.) determined what thickness of silver it is necessary to deposit on glass so that the capillary effect on water may be the same as that of solid silver; that is, at what distance the difference between the molecular attractions of glass and silver for water becomes too small to be measured. He found the thickness to be about 50 micromms.

Now, according to the law of the inverse fourth power, the attraction of a cylinder of radius c, length h, and density ρ on a particle of mass m on the axis at a distance z from the nearest end is easily calculated as

$$2\mathrm{A}m\rho\pi\left(\frac{1}{z} - \frac{1}{z+h} - \frac{1}{\sqrt{c^2+z^2}} + \frac{1}{\sqrt{c^2+(z+h)^2}}\right).$$

If the cylinder consists of a length h_1 of silver with a length h_2 of glass, the silver being near the particle, then, the suffixes 1 and 2 applying to silver and glass, the attraction of the composite cylinder is

$$2\mathrm{A}_1 m\rho_1 \frac{\pi}{z} - 2m\pi(\mathrm{A}_1\rho_1 - \mathrm{A}_2\rho_2)\left(\frac{1}{z+h_1} - \frac{1}{\sqrt{c^2+(z+h_1)^2}}\right)$$

$$-2\mathrm{A}_1 m\rho_1 \frac{\pi}{\sqrt{c^2+z^2}} - 2\mathrm{A}_2 m\rho_2\pi\left(\frac{1}{z+h_1+h_2} - \frac{1}{\sqrt{c^2+(z+h_1+h_2)^2}}\right)$$

Making the circumstances correspond to Quincke's experiment, we have z nearly equal to the mean molecular distance in water, about 10 micromms.; h_1 is small compared to h_2 and c, and, according to Quincke, is 50 micromms. when the composite cylinder exerts the same force on m as if it were all silver; accordingly the last expression reduces to the two terms

$$2\mathrm{A}_1 m\rho_1\pi/z - 2m\pi(\mathrm{A}_1\rho_1 - \mathrm{A}_2\rho_2)/(z+h_1),$$

which permit us to compare the molecular force range h_1 with the molecular distance z. That the second of these terms should become negligible when h_1 is 50 micromms. is a result quite in accordance with the value 10 micromms. for z.

Let us briefly compare the magnitudes of molecular and gravitational force. The most convenient plan will be to compare the two forces in the case of two single ethyl-oxide

molecules at a distance of one centim. apart; that is, to calculate Am^2 and Gm^2, where m is the actual mass of the molecule, and G the constant in the expression Gm^2/r^2 for gravitation.

In the expression

$$\alpha = \pi\bar{\rho}^2 Ax/2\cdot 2(2+\sqrt{2}),$$

using the value 10 micromms. for x and the values previously given for the other quantities, we can find A, and then using the value $3\cdot 5/10^{19}$ for the mass of a molecule of ethyl oxide we find $Am^2 = 9/10^{30}$ in terms of the dyne. To calculate G we have 981 as the acceleration of gravitation; the mass of the earth is 6×10^9 grm. and its radius is $6\cdot 37\times 10^7$cm., so that $Gm^2 = 2\cdot 1/10^{29}$ in terms of the dyne. Hence at a distance of 1 centim. the gravitation of two ethyl-oxide molecules is about double their molecular attraction, or, allowing for uncertainties in our calculation, we may say that at about 1 centim. apart two molecules exert the same gravitational as molecular force on one another.

We now return to the main business of this section, which is the *Fifth Method* of finding the virial constant l. This consists in using the equation already used for calculating molecular distances in the form

$$l = 7\cdot 5v^2\alpha(4\log 2L/\cdot 9x - 16/3)\big/x.$$

Now x, the molecular distance for different liquids, varies as $m^{\frac{1}{3}}v^{\frac{1}{3}}$, and the expression in brackets may be assumed to be the same for all bodies; hence $l = c\alpha v^{\frac{5}{3}}/m^{\frac{1}{3}}$, where c is a constant whose value can be obtained on substituting in the case of ethyl oxide the known values of l, α, v, and m, or, more safely, by taking a mean value from several substances.

But we must remember that we are using v the volume in the body of the liquid, instead of $\bar{v}$ that in the surface-film; a replacement which is not justified by experiment, seeing that for a given liquid $\alpha v^{\frac{5}{3}}$ measured at different temperatures is not constant, the reason being that $\bar{v}$ varies much more rapidly with temperature than v. But, in our ignorance of the relation between surface and body-density, all that we seek for from the above equation for l, is true values for l from measured values for α. Accordingly the question arises, Can we choose temperatures at which to measure α for different substances, so as to get true relative values of l irrespective of our ignorance of $\bar{v}$?

As we have seen (Section 6) that at equal fractions of their critical temperatures, and under equal fractions of their critical pressures, one liquid is approximately a model of another on

a different scale, we conclude that if we use the value of the surface-tension measured at a constant fraction of the critical temperature, and under a constant fraction of the critical pressure, we ought to get correct relative values of l; as surface-tension is not appreciably affected by pressure, we can dispense with the condition as to pressure and use measurements of α made under a pressure of one atmosphere at a constant fraction of the critical temperature. I have chosen the fraction as two-thirds, because it gives a temperature near to the boiling-point of most liquids.

Schiff's abundant measurements (*Ann. der Chem.* ccxxiii., and, further, Wied. *Beibl.* ix.) include not only the height to which different liquids rise in a capillary tube at their boiling-points, but also its temperature-coefficient, which is such as to show that the height in every case vanishes near the critical point.

Let H be the height to which a liquid rises in a tube of radius 1 millim.; then if H really vanished at the critical temperature and varied linearly with temperature, we should at $2T_c/3$ have $H=T_cb/3$, where b is the temperature-coefficient. But to use this would be to depend too much on the accuracy of b.

If H_b is the value at T_b the boiling-point, then $T_c=T_b+H_b/b$, and

$$H=H_b+(T_b-2T_c/3)b=H_b/3+T_bb/3,$$

which depends partly on H_b, measured by Schiff, and partly on b. Now $\alpha=H\rho/2=H/2v$;

$$\therefore\ l \text{ or } c\alpha v^{\frac{5}{3}}/m^{\frac{1}{3}}=cHv^{\frac{2}{3}}/2m^{\frac{1}{3}},$$

$$l=c(H_b/3+T_bb/3)v^{\frac{2}{3}}/2m^{\frac{1}{3}}.$$

If H is measured according to the usual practice as the height in millimetres for a tube of radius 1 millim., that is, if α is measured in grammes weight per metre, then if l is desired in terms of the megadyne, gramme, and centimetre as units, $c/2=5930$, a mean value. Apart from all hypothesis about molecular force, our last relation between the virial constant and the constants of capillarity will be amply confirmed by the extensive comparisons soon to be presented in Tables XXIV. and XXV. Meanwhile a few consequences of the relation may be glanced at.

9. *Establishment on Theoretical grounds of Eötvös's relation between surface-tension, volume, and temperature.*—According to the modified equation of the fourth method of finding l, $Ml=800T_cv_1$; and according to that of the fifth method, $l=c\alpha v^{\frac{5}{3}}/m^{\frac{1}{3}}$. The first of these equations would be more accurate if we replaced v_1 by v, which in the second means the volume at $2T_c/3$; so $Ml=800T_cv$, and m the actual mass

of the molecule is proportional to M its molecular weight; so that from the second we have Ml proportional to $\alpha(Mv)^{\frac{2}{3}}v$, and hence $\alpha(Mv)^{\frac{2}{3}}$ measured at $2T_c/3$ is for all bodies proportional to T_c. Now in our notation the relation discovered by Eötvös (Wied. *Ann.* xxvii.) is

$$d\{\alpha(Mv)^{\frac{2}{3}}\}/dT = \cdot 227,$$

or

$$\alpha(Mv)^{\frac{2}{3}} = \cdot 227(T - T_c'),$$

where T_c' is a temperature very close to the critical; and this is only a more general statement of the relation we have just deduced.

As Eötvös has verified his relation experimentally for a large number of bodies, his result is a verification also of our general principles. The form of his relation also induces us to examine a little more closely an important consequence of the form of our infracritical equation, which, when multiplied by M with the pv term removed at low pressures, becomes

$$\frac{Ml}{2v} = R'M\left(1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta}\right)T.$$

Now $R'M$ is constant, and Ml/v is proportional to $\alpha(Mv)^{\frac{2}{3}}$, if α and v are measured at $2T_c/3$, or any other constant fraction of the critical temperature, and under these circumstances $\alpha(Mv)^{\frac{2}{3}}$ has been shown to be proportional to T_c; hence if T is aT_c, a being a constant fraction, we get T_c proportional to

$$\left(1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta}\right) aT_c,$$

so that $1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta}$, measured at a constant fraction of the critical temperature, is approximately the same for all bodies, a result which our study of Van der Waals's generalization showed us to be approximately true. This shows that Eötvös's relation is rigorous only to the same extent as the constancy of this last expression is rigorous; as a matter of fact, excluding the alcohols and water, Eötvös finds the constant whose mean value is taken as ·227 to depart from this mean value by not more than 5 per cent. in any individual case. This brief discussion of Eötvös's relation has therefore furnished us with additional proof of the general accuracy of the approximations we have been forced to make in parts of our work.

One of the main difficulties in the way of pushing on with the many interesting inquiries opened up by these relations lies in the fact that we do not know the relation between the densities in the body and in the surface-layer of a liquid.

We have to replace our relation

$$\alpha \text{ varies as } A\bar{\rho}^{\frac{5}{3}}m^{\frac{1}{3}}$$

by the less accurate one,

$$\alpha \text{ varies as } A\rho^{\frac{5}{3}}m^{\frac{1}{3}}.$$

Multiplying by $(Mv)^{\frac{2}{3}}$ or $(M/\rho)^{\frac{2}{3}}$, we get the $\alpha(Mv)^{\frac{2}{3}}$ of Eötvös proportional at all temperatures to $AM\rho$; and as $d\{\alpha(Mv)^{\frac{2}{3}}\}dT$ is constant, and has been shown by Eötvös to be constant almost right up to the critical temperature, and to be the same for all bodies, we ought, if our assumptions were rigorous, to have $AMd\rho/dT$ constant almost up to the critical temperature and the same for all bodies (whence another approximate method of finding A or l). Now $d\rho/dT$ has been shown by Mendeléeff to be constant for many substances within ordinary temperature-ranges; but the constancy does not hold up to the critical temperature, and the ultimate meaning of the apparent contradiction between Eötvös's result and this is that, while for most purposes we may safely enough assume $\bar{\rho}$ proportional to ρ, we cannot so accurately proceed to the consequence $d\bar{\rho}^{\frac{5}{3}}/dT$ proportional to $d\rho^{\frac{5}{3}}/dT$; in fact, a change of temperature being accompanied by a change of stress in the surface-layer, the change of $\bar{\rho}$ with temperature is more complex than that of ρ. But within the range of temperature for which $d\rho/dT$ is approximately constant, we have the important result that

$$\frac{d}{dT}MR'\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)T$$

is constant and is approximately the same for all bodies.

As I now consider the term differentiated to be not two thirds of the translatory kinetic energy of the gramme-molecule, but two thirds of the sum of the total kinetic energy and the chemic virial, I must replace the verbal statement of the last result as given in my paper (Phil. Mag. April 1889, p. 312) by the following:—The temperature-rate of variation of the sum of the total kinetic energy and the chemic virial of a molecule, measured at low constant pressure, is the same for all bodies (approximately).

10. *Tabulation of Values of the Virial Constant*, determined by four of the five methods described, and multiplied by the square of the molecular weight.—In the first place, I will give a comparison of the values of M^2l for those bodies to which existing data allow the application of three or four of the previously described methods. The multiplication by M^2 is for future convenience. The values obtained by the second

(liquid compression and expansion), third (latent heat), fourth (critical temperature), and fifth (capillarity) methods are entered in the columns marked 2, 3, 4, and 5. (The modified fourth method was used, namely, $Ml = 800\,T_c v_1$.)

The units are the megamegadyne (10^{12} dynes), grm., and cm.

TABLE XXIV.

Substance.	2.	3.	4.	5.
CS_2	26·5	25·7	27·2	26·9
PCl_3	.....	39·7	41·7	43·4
CCl_4	.....	46·3	46·2	45·6
$CHCl_3$	33·0	38·2	36·1	36·8
C_2H_5Cl	22·3	28·3	26·5	
C_2H_5Br	.....	32·1	31·5	29·0
C_5H_{12}	48·0	.....	45·3	47·1
C_6H_{14}	57·0	.....	58·5	59·3
C_6H_6	40·0	43·1	42·7	43·8
C_7H_8	59·0	55·8	56·2	56·4
$(CH_3)_2CO$	.....	36·0	31·3	31·1
Methyl butyrate	65·0	60·4	55·6	56·1
Ethyl butyrate	84·0	74·6	69·5	71·3

The satisfactory agreement of these values, calculated for such diverse bodies from such diverse data, must be taken as the verification of the main principles so far unfolded—the chief of which as regards molecular force is that for most compound bodies the internal virial term of the characteristic equation is $l/2v$ below the volume k, and $l/(v+k)$ above that volume.

We see, too, now how important for molecular dynamics is the detailed study of each of the constants k, B, and β in the characteristic equations; but for the present we must refrain from entering on such a study, and must consider the comparison in the last table as closing for the present the general discussion of the characteristic equation.

Our immediate object is now to ascertain the law connecting the value of M^2l for a body with its chemical composition. On the hypothesis of the inverse fourth power (with the subsidiary one of molecular swarms),

$$m^2l = \pi m^2 A(4 \log 2L/a - 16/3)\,;$$

so that, the bracketed expression being the same for all bodies, m^2l is proportional to m^2A, and the law of m^2l or M^2l will be the law of m^2A in the expression $3Am^2/r^4$ for the force between two molecules. In the Phil. Mag. for April 1889 I announced a law for the parameter A, calculated from Schiff's capillary data, which applied fairly well to a large number of organic compounds, but was affected with exceptions subversive of its generality. Applying now the more accurate method of

calculation described as the fifth to all Schiff's data, we obtain ample material for generalization, which can be supplemented by values calculated by the other methods.

In the following Table the units are again the megamegadyne, grm., and cm. For brevity the radicals methyl, ethyl, and propyl, &c., will be denoted by the first two letters of their names, while the acid radicals—formic, propionic, &c.—will be denoted by Fot, Prt, and so on, so that PrPrt stands for propyl propionate. The numbers entered under the heading S will be explained when we are discussing the law of M^2l.

TABLE XXV.—Values of M^2l.

First Method.					
	M^2l.	S.		M^2l.	S.
Et_2O	40·2	4·5	H_2	·22	·04
CO_2	7·1	1·07	N_2	1·23	·205
SO_2	15·0	2·05	O_2	1·16	·195
NH_3	8·5	1·25	CH_4	2·2	·35
N_2O	8·8	1·3	C_2H_4	6·5	1·0

Third Method.					
	M^2l.	S.		M^2l.	S.
$SnCl_4$	61·3	6·1	IsoBuAct	76·2	7·1
$AsCl_3$	49·0	5·2	EtBut	76·9	7·15
BCl_3	23·5	2·95	PrPrt	77·3	7·2
$SiCl_4$	47·3	5·05	IsoAmFot	78·7	7·3
CH_3I	27·4	3·3	PrisoBut	89·1	8·0
EtI	40·0	4·5	EtVat	89·5	8·0
$AmI(C_5H_{11}I)$	88·3	7·9	IsoBuPrt	92·5	8·15
AmBr	61·8	6·15	IsoAmAct	93·1	8·15
AmCl	48·7	5·15	PrBut	92·5	8·15
C_5H_{10}	35·0	4·0	IsoBuisoBut	105	8·9
$C_{10}H_{20}$	90·4	8·0	PrVat	106	8·9
$C_{10}H_{16}$	109·0	9·1	IsoBuBut	109	9·1
$C_2H_4Br_2$	49·4	5·2	IsoAmPrt	110	9·15
$Et_2C_2O_4$	109·0	9·1	IsoAmisoBut	125	9·95
Et_2O	44·1	4·8	IsoPrVat	126	10
EtFot	35·6	4·1	IsoAmBut	129	10·15
MeAct	36·0	4·1	IsoAmVat	147	11
EtAct	47·6	5·1	C_6H_6	43·1	4·7
MePrt	47·5	5·1	C_7H_8	55·8	5·7
PrFot	50·2	5·3	C_6H_5Et	69·5	6·65
MeButiso	60·4	6·04	C_8H_{10} (meta)	71·4	6·8
IsoBuFot	63·7	6·3	C_6H_5Pr	85·9	7·75
EtPrt	62·4	6·2	C_9H_{12}(mesitylene)	86·1	7·75
PrAct	62·8	6·2	C_9H_{12} (pseudo-cumene)	87·1	7·8
MeBut	61·8	6·15			
EtisoBut	74·6	7·0	$C_{10}H_{14}$ (cymene)	101	8·6
MeVat	74·1	7·0			

Table XXV. (*continued*).

Fourth Method.

	M^2l.	S.		M^2l.	S.
Cl_2	5·8	·9	PrCl	34·6	4·0
H_2S	10·5	1·5	NH_3	10·0	1·4
C_2H_2	9·8	1·4	NH_2Me	17·6	2·3
C_2H_6	14·7	2·0	$NHMe_2$	23·5	3·0
C_5H_{10}	44·1	4·8	NMe_3	31·6	3·7
$CHCl_3$	36·9	4·2	NH_2Et	21·2	2·7
CS_2	27·0	3·3	$NHEt_2$	41·4	4·55
C_2N_2	17·7	2·3	NEt_3	65·5	6·4
HCl	7·9	1·15	NH_2Pr	33·4	3·9
CH_3Cl	15·6	2·1	$NHPr_2$	67·6	6·5
EtCl	26·6	3·25			

Fourth Method modified (not using critical pressures).

	M^2l.	S.		M^2l.	S.
$(CH_2Cl)_2$	38·0	4·3	EtC_3H_5O	48·6	5·15
CH_3CHCl_2	37·7	4·3	HCl	7·3	1·1
C_3H_5Cl	34·0	4·0	MeCl	16·8	2·2
$CH_2(OCH_3)_2$ (methylal)	38·5	4·3	EtCl	26·4	3·2
			PrCl	32·6	3·8
$CH_3CH(OC_2H_5)_2$ (acetal)	68·7	6·6	NH_3	7·6	1·1
			NH_2Me	15·6	2·1
C_5H_{10}	41·8	4·6	$NHMe_2$	23·5	3·0
C_6H_{10}	51·2	5·4	NMe_3	31·0	3·7
C_8H_{18}	80·5	7·4	NH_2Et	24·4	3·05
C_8H_{16}	81·1	7·4	$NHEt_2$	43·5	4·75
Me_2O	20·3	2·6	NEt_3	66·4	6·5
MeEtO	29·9	3·6	NH_2Pr	31·0	3·7
EtPrO	52·4	5·45	$NHPr_2$	68·6	6·6

Fifth Method.

	M^2l.	S.		M^2l.	S.
EtFot	32·1	3·8	EtBut	72·3	6·85
MeAct	35·6	4·1	EtisoBut	71·3	6·8
PrFot	44·2	4·8	MeVat	69·7	6·7
EtAct	45·4	4·9	IsoAmAct	87·3	7·8
MePrt	44·8	4·85	IsoBuPrt	87·7	7·85
IsoBuFot	56·9	5·8	PrBut	89·3	7·95
PrAct	57·9	5·85	PrisoBut	87·7	7·85
EtPrt	58·5	5·9	EtisoVat	86·5	7·8
MeBut	58·2	5·9	IsoAmPrt	105	8·85
MeisoBut	56·1	5·75	IsoBuBut	106	8·9
IsoAmFot	71·6	6·8	IsoBuisoBut	103	8·75
IsoBuAct	70·6	6·75	PrisoVat	103	8·75
PrPrt	73·3	6·9			

Table XXV. (*continued*).

		M^2l.	S.
C_6H_{14}	Normal hexane	59·3	6·0
C_8H_{18}	Diisobutyl	90·6	8·0
$C_{10}H_{22}$	Diisoamyl	125·6	10·0
C_5H_{10}	Amylene	45·0	4·9
C_8H_{16}	Caprylene	91·8	8·1
$C_{10}H_{16}$	Terpene	107·4	9·0
C_6H_{10}	Diallyl	54·8	5·6
C_6H_6	Benzene	43·8	4·75
C_7H_8	Toluene	56·4	5·75
C_8H_{10}	Orthoxylene	69·7	6·65
C_8H_{10}	Metaxylene	69·7	6·65
C_8H_{10}	Paraxylene	70·3	6·7
C_8H_{10}	Ethylbenzene	70·6	6·7
C_9H_{12}	Normal propylbenzene	86·9	7·8
C_9H_{12}	Ethyltoluene	86·1	7·75
C_9H_{12}	Mesitylene	85·3	7·65
$C_{10}H_{14}$	Cymene	103·0	8·75
$CHCl_3$	Chloroform	36·9	4·2
CCl_4	Carbon tetrachloride	45·6	4·9
$(CH_2Cl)_2$	Ethylene chloride	44·4	4·8
CH_3CHCl_2	Ethidene chloride	38·1	4·3
PrCl	Propyl chloride	37·9	4·3
IsoBuCl	Isobutyl chloride	52·0	5·4
IsoAmCl	Isoamyl chloride	66·4	6·45
C_6H_5Cl	Chlorobenzene	57·7	5·85
C_7H_7Cl	Chlorotoluene	76·0	7 1
C_7H_7Cl	Benzyl chloride	82·2	7·5
$C_3H_6Cl_2$	Propylene chloride	56·8	5·8
C_2Cl_4	.....	65·6	6·4
$C_2H_3Cl_3$	Trichlorethane	58·2	5·9
C_3H_5ClO	Epichlorhydrin	49·8	5·25
CCl_3COH	Chloral	50·9	5·35
CH_2ClCO_2Et	Ethyl chloracetate	63·2	6·25
$CHCl_2CO_2Et$	Ethyl dichloracetate	79·6	7·35
CCl_3CO_2Et	Ethyl trichloracetate	93·5	8·2
C_7H_5OCl	Benzoic chloride	79·6	7·35
$C_7H_6Cl_2$	Benzilidene chloride	89·4	8·0
EtBr	Ethyl bromide	28·9	3·5
PrBr	Propyl bromide	41·4	4·6
IsoPrBr	Isopropyl bromide	41·2	4·6
C_3H_5Br	Allyl bromide	39·9	4·45
IsoBuBr	Isobutyl bromide	53·3	5·5
IsoAmBr	Isoamyl bromide	66·2	6·45
C_6H_5Br	Bromobenzene	66·8	6·5
C_7H_7Br	Orthobromotoluene	81·5	7·45
$C_2H_4Br_2$	Ethylene bromide	51·2	5·35
$C_3H_6Br_2$	Propylene bromide	61·5	6·1
MeI	Methyl iodide	25·6	3·15
EtI	Ethyl iodide	38·1	4·3
PrI	Propyl iodide	50·9	5·3
IsoPrI	Isopropyl iodide	49·8	5·25
C_3H_5I	Allyl iodide	50·2	5·3
IsoBuI	Isobutyl iodide	62·4	6·2
IsoAmI	Isoamyl iodide	80·0	7·35

Table XXV. (*continued*).

		M^2l.	S.
C_6H_5I	Iodobenzene	80·4	7·35
NH_2Pr	Propyl amine	37·8	4·25
$NH_2C_3H_5$	Allyl amine	36·6	4·2
NH_2isoBu	Isobutyl amine	50·6	5·3
NH_2isoAm	Isoamyl amine	64·4	6·3
$NHEt_2$	Diethyl amine	50·1	5·5
NEt_3	Triethyl amine	75·2	7·05
$NH_2C_6H_5$	Aniline	65·0	6·35
C_5H_5N	Pyridine	59·7	6·0
C_9H_7N	Piperidine	100·3	8·6
C_9H_7N	Chinoline	108·6	9·05
$MeNO_2$	Nitromethane	22·6	2·75
CCl_3NO_2	Chloropicrin	57·6	5·85
$EtNO_3$	Ethyl nitrate	37·2	4·2
$IsoAmNO_3$	Isoamyl nitrate	76·9	7·2
C_3H_7CN	Isobutylnitrile	39·2	4·4
C_4H_9CN	Capronitrile	50·5	5·3
C_6H_5CN	Benzonitrile	65·8	6·4
CS_2	Carbon disulphide	26·9	3·3
$CSNC_3H_5$	Allyl sulphocarbimid	54·0	5·55
$CNSCH_3$	Methyl sulphocyanate	33·7	3·9
$CNSC_2H_5$	Ethyl sulphocyanate	44·1	4·8
Et_2S	Ethyl sulphide	55·0	5·6
PCl_3	.....	43·4	4·75
$POCl$	.....	25·0	3·1
POC_2H_5Cl	Ethoxyphosph. chloride	62·8	6·2
$PSCl$	.....	35·5	4·1
$(CH_3)_2CO$	Acetone	31·1	3·7
$C_6H_{12}O_3$	Paraldehyde	85·7	7·7
$CH_3CH(OCH_3)_2$	Dimethylacetal	53·3	5·5
$CH_3CH(OC_2H_5)_2$	Diethylacetal	87·7	7·85
Et_2O	Ethyl oxide	43·8	4·75
$(CH_3CO)_2O$	Acetic anhydride	51·9	5·4
$CH_3CO_2C_3H_5$	Allyl acetate	54·1	5·55
$MeisoAmO$	Methylisoamyl oxide	66·8	6·5
$Et_2C_2O_4$	Ethyl oxalate	91·0	8·05
$C_6H_5CO_2CH_3$	Methyl benzoate	91·4	8·1
$C_6H_5CO_2C_2H_5$	Ethyl benzoate	109·9	9·15
$CH_3(CO)_2CH_2OEt$	Acetacetic ether	81·5	7·45
$C_6H_5OCH_3$	Anisol	70·0	6·7
$C_6H_5OC_2H_5$	Phenethol	80·7	7·4
$C_7H_7OCH_3$	Methyl paracresolate	84·1	7·6
$C_6H_4(OCH_3)_2$	Dimethyl resorcin	96·2	8·35
C_4H_2OHCOH	Furfurol	51·2	5·3
C_4H_9COH	Valeraldehyde	48·0	5·1
$C_9H_{11}COH$	Cuminol	113·0	9·3
$C_{10}H_{14}O$	Carvol	117·8	9·6
$(CH_3)_3CCOCH_3$	Pinakoline	63·5	6·3

The following are the chief sources of the data from which the above table has been constructed:—Latent Heats from Berthelot (*Chimie Mécanique*) and R. Schiff (*Ann. der Chem.* ccxxxiv.). Critical Temperatures from Sajontschewski (Wied. *Beibl.* iii.), Pawlewski (*Ber. deut. chem. Ges.* xv., xvi.), Nadejdine (Wied. *Beibl.* vii.), and Dewar (Phil. Mag. xviii.). Surface-tensions from R. Schiff (*Ann. der Chem.* ccxxiii.; Wied. *Beibl.* ix.).

To make clear the two simple laws that rule these tabulated values, it will be advisable to confine our attention at first only to those values obtained by the fifth method, using those by other methods only to fill gaps. It will also be well to consider first a single chemical family, such as the paraffins, for which we have the following values :—

CH_4.	C_2H_6.	C_6H_{14}.	C_8H_{18}.	$C_{10}H_{22}$.
2·2	14·7	59·3	90·6	125·6

These show that there is not a constant difference in the value of M^2l corresponding to the difference in the number of CH_2 groups contained. We can amplify this list of paraffins by using the material furnished by Bartoli and Stracciati (*Ann. de Chim. et de Phys.* sér. 6, t. vii.), who have determined the more important physical constants for all the paraffins from C_5H_{12} up to $C_{16}H_{34}$. Their values of the capillary constants were found at about 11 degrees in every case. To obtain those at two thirds of the critical temperature, we have to use the values of the critical temperatures calculated by them from Thorpe and Rücker's convenient empirical relation (Journ. Chem. Soc. xlv.),

$$\rho/(2T_c - T) = \text{constant},$$

ρ being density at T.

The following are the values of M^2l thus obtained :—

C_5H_{12}.	C_6H_{14}.	C_7H_{16}.	C_7H_{16}.	C_8H_{18}.	C_9H_{20}.	$C_{10}H_{22}$.
47·2	58 1	77·1	79·6	91·2	110	127

$C_{11}H_{24}$.	$C_{12}H_{26}$.	$C_{13}H_{28}$.	$C_{14}H_{30}$.	$C_{15}H_{32}$.	$C_{16}H_{34}$.
147	171	192	215	230	256

Considering the assumptions involved in the calculation of these values and the difficulty of obtaining the paraffins pure, the agreement for C_6H_{14}, C_8H_{18}, and $C_{10}H_{22}$ with Schiff's numbers is excellent; but the higher we go in the series the larger is the temperature-interval for which we have to extrapolate, and the more uncertain do the values become. However, they are useful as giving a general idea of the course of M^2l in an extended series.

On plotting these numbers as ordinates with abscissæ representing the number of CH_2 groups in the molecule, a curve was constructed which proved to be the parabola

$$M^2l = 6S + \cdot 66S^2,$$

where S is the number of CH_2 groups. It is only necessary then to determine on this curve the abscissa corresponding to

the value of M^2l for any substance to obtain the number of CH_2 groups to which its molecule is equivalent as regards molecular force.

11. *Definition of the Dynic Equivalent of a substance, and determination of its value for several Radicals.*—In the manner just described were obtained the numbers entered in Table XXV. under the heading S, which I propose to call the Dynic Equivalents of the substances. The dynic equivalent of a molecule is the number of CH_2 groups in the molecule of the normal paraffin that exerts the same molecular force as it.

The table shows that the atom of an element contributes the same amount towards the dynic equivalent of all molecules in which it occurs (except in the case of the simpler typical compounds) : thus, for example, consider the iodides from methyl to amyl iodide, and notice that each CH_2 group has the same value unity as in the paraffins, and that the iodine atom is equivalent to about $2{\cdot}3CH_2$ in every case. The same law holds throughout the table ; so that each elementary atom or radical has its own dynic equivalent, which can be easily determined.

In the first place, it appears that the extra H_2 in the paraffins C_nH_{2n+2} can be neglected in a first approximation, because C_5H_{10} has practically the same dynic equivalent as C_5H_{12}, and C_8H_{16} the same as C_8H_{18}. It may be that the double binding in the unsaturated compounds compensates for the H_2 of the saturated, but I think that the simpler idea for the present is that the two terminal H atoms in a paraffin chain have a dynic equivalent so small that we may neglect it, or more generally the middle H in a CH_3 group is negligible in a first approximation. If there is really such a difference between the middle H and the two others in CH_3, we ought to find the dynic equivalents for the iso-compounds smaller than for the normal ; and the table shows that the isobutyrates have equivalents smaller by ·1 than the butyrates, while the isobutyl salts of the fatty acids have dynic equivalents nearly all less than 1 greater than the propyl salts. But this is rather a matter for the chemist to work out in detail ; it suffices to indicate the idea here, and to point out that it is in harmony with the lowering of boiling-points among isomers with increasing number of CH_3 groups. Accordingly, as a matter of detail, in the estimation of the dynic equivalents of the elements, it was assumed that the equivalent of C_nH_{2n+2}, C_nH_{2n+1}, and C_nH_{2n} is in each case n when normal and $n-{\cdot}1p$ when the molecule departs from normality by p CH_3 groups. (In constructing my curve for dynic equivalents, for the sake of

simplicity at first, I ignored the fact that two of the paraffins in Schiff's data are iso-compounds.)

From the tabulated values for the alkyl salts of the fatty acids, we get the following mean values for the dynic equivalent of $CO''O'$:—in the formiates 1·85, acetates 1·92, propionates 1·91, butyrates 1·92, isobutyrates 1·91, and isovalerates 1·83, the mean for all being 1·9.

From the oxides (ethers) and other compounds containing single-bound O, we find for its mean value ·6, although in the ethers containing the benzene nucleus it comes out ·8, while in the benzoates $CO''O'$ is about 2·5 ; so that the junction of the benzene nucleus with other groups seems to be accompanied with an increase in its value : witness also the bromide, iodide, and amine of C_6H_5, equal to the bromide, iodide, and amine of C_5H_{11}, although C_6H_6 is less than C_5H_{12} by ·25. This slight variation of the value of C_6H_6 is the only anomaly amongst the numbers of Table XXV. excepting the simple typical compounds. The values ·6 for O' and 1·9 for $C''O'$ are in harmony with the results for all the other compounds containing oxygen.

From the values for the benzene series of hydrocarbons we can get a value for H_2 in CH_2, and also some light on the important question of the structure of the benzene nucleus. Thomsen has been led by his thermochemical investigations to the conclusion that in benzene each carbon atom is bound to three other carbon atoms by a single bond to each (the "bond" phraseology is used merely for brevity, and not as expressing definite statical or dynamical facts). If we accept this conclusion, then the dynic equivalent of C_6H_{12} minus that for C_6H_6 is equal to the dynic equivalent of $3H_2$; similarly, from the other members of the benzene series we get the values for $3H_2$, the mean result being 1·29 or ·43 for H_2.

The accepted structure for C_6H_{10} diallyl is $(CH_2CHCH_2)_2$, or four whole CH_2 groups and two CH_2 groups with H removed from each ; and as the dynic equivalent of C_6H_{10} is 5·6, we find that of H_2 to be ·4. Again, recent investigations on the terpenes (Wallach, *Ann. der Chem.* ccxxv., ccxxvii., ccxxx.; Brühl, ccxxxv.) show that the two ordinary forms can have their formulæ written $CH_3C_3H_7(CH_2)_2(CH)_2C_2$; that is to say, they have 6 hydrogen atoms cut out of CH_2 groups, and as the dynic equivalent of $C_{10}H_{16}$ is 9 we have that of $3H_2$ as 1·0 or that of H_2 ·33. Since the value ·43 is derived from 10 accordant members of the benzene series, we will take it as the value of the dynic equivalent of H_2 in CH_2.

By similar but simpler reasoning the dynic equivalents of Cl, Br, I, and other radicals are easily found, and the following is a list of mean values :—

TABLE XXVI.—Dynic Equivalents.

CH_2.	H.	C.	C″O′.	O′.	NH_2.	CN.
1·0	·215	·57	1·9	·6	1·23	1·35

NO_3.	CNS.	S′.	Cl.	Br.	I.
2·2	2·85	1·6	1·3	1·6	2·3

To illustrate the applicability of these values, I furnish a comparison of the values calculated by means of them for twenty substances with the values tabulated in Table XXV.

TABLE XXVII.

Comparison of calculated and tabulated Dynic Equivalents.

	Calc.	Tab.		Calc.	Tab.
C_6H_6	4·8	4·75	C_4H_9CN.....	5·35	5·3
$C_{10}H_{14}$	8·8	8·75	$C_4H_{10}S$	5·6	5·6
C_3H_7Cl	4·3	4·3	C_2H_5CNS	4·85	4·8
$C_5H_{11}Cl$	6·3	6·45	$(CH_3)_2O$.....	2·6	2·6
C_2H_5Br	3·6	3·5	$CH_3C_5H_{11}O$	6·6	6·5
$C_5H_{11}Br$.....	6·6	6·45	$C_6H_{12}O_3$.....	7·8	7·7
C_2H_5I.....	4·3	4·3	$(CH_3CO)_2O$	5·2	5·4
$C_5H_{11}I$	7·3	7·35	C_4H_9COH.....	5·3	5·1
$NH_2C_3H_7$	4·23	4·25	$C_4H_8O_2$	4·9	4·9
$NH_2C_5H_{11}$	6·23	6·3	$C_7H_{14}O_2$.....	7·9	7·9

If we now look at the dynic equivalents of the uncombined elements given in the first part of Table XXV., we may notice that they are remarkably small compared to the values in the combined state; thus, that of H_2 is ·04, of N_2 ·205, of O_2 ·195, and that of CH_4 is small too, ·35, instead of 1 as it should be, seeing that CH_4 is the first of the paraffin series. Other typical compounds have small values: CO_2 has 1·05, while C″O′ in more elaborate compounds has a value 1·9, C_2H_4 has 1, while C_2H_6 has 2; and so on. The same fact has been noticed in connexion with the molecular refraction of some of the typical compounds and some of their immediate derivatives, and it will yet prove a most important one in chemical dynamics. But meanwhile it is of greater importance

for present purposes to notice that the dynic equivalents given for various radicals in Table XXVI. are closely proportional to their molecular refractions.

12. *Close parallelism between Dynic Equivalents and Molecular Refractions.*—As is well known, there are two methods according to which the molecular refraction is estimated, the first by means of Gladstone's expression, $(n-1)M/\rho$, where n is index of refraction; the other by means of Lorenz's, $(n^2-1)M/(n^2+2)\rho$.

In a brief paper (Phil. Mag. Feb. 1889) I showed that the experimental evidence taken as a whole is in favour of the Gladstone expression, for which also a very simple theoretical proof can be given; and, further, it was shown that it is best to measure $(n-1)M/\rho$ if possible in the gaseous state. But as comparatively few measurements have been made on bodies in the vapour state I suggested that, as the Lorenz expression had been empirically proved to give more nearly the same value in the liquid and vapour states of a body, its value as determined in the liquid state and multiplied by 3/2 could be taken as giving the value of $(n-1)M/\rho$ in the vapour state. The result of the theoretical argument was that, if M/ρ is taken to measure the molecular domain u, and if U is the volume occupied by the molecule in the same units, and N is the index of refraction for the matter of the molecule, then

$$(n-1)u = (N-1)U.$$

Landolt, Brühl, and others have determined the values of the atomic refraction for several elements (*Ann. der Chem.* ccxiii. p. 235), and by means of these and Masini's data for sulphur (Wied. *Beibl.* vii.) and Gladstone's latest determinations (Journ. Chem. Soc. 1884), I have obtained the values of the refraction-equivalents of the preceding radicals in terms of that for CH_2 as unity. Mascart has given (*Compt. Rend.* lxxxvi.) values of the refraction of a number of substances in the vapour state, from which, for the sake of comparison, I have calculated the refraction-equivalents for as many radicals as possible.

The following Table contains in the second column the dynic equivalent, in the third the refraction-equivalent calculated according to the Lorenz expression, in the fourth the refraction-equivalent calculated according to the Gladstone expression from Mascart's data for vapours, and in the fifth that calculated by Gladstone from liquid data. The value for CH_2 in every case is 1.

TABLE XXVIII.

Comparison of Dynic and Refraction Equivalents.

1.	2.	3.	4.	5.
CH_2	1·0	1·0	1·0	1·0
H	·215	·23	·19	·17
C	·57	·54	·62	·66
CO″O′	1·9	1·4	1·5	1·5
O′	·6	·35	·4	·37
NH_2	1·23	1·12	.....	1·01
CN.....	1·35	1·18	1·3	1·2
NO_3	2·2	2·2	.....	1·9
CNS	2·85	.....	.....	3·0
S′	1·6	1·7	.....	1·9
Cl	1·3	1·3	1·5	1·3
Br	1·6	2·0	1·7	2·0
I.....	2·3	3·1	2·7	3·2

This table brings out the remarkable fact that the parallelism between the dynic and refraction-equivalents is so close as almost to amount to proportionality. I shall not discuss the meaning of this relation until I have shown how to obtain the dynic equivalents for the elements usually occurring in inorganic compounds, and established the same relation for them also.

Meanwhile it will be useful to compare the dynic and refraction equivalents of the uncombined elements and of those simpler typical compounds to which we have said the summative law does not apply as regards dynic equivalents and does not accurately apply as regards refraction-equivalents.

TABLE XXIX.

Ratio of Dynic to Refraction Equivalents, each measured in terms of that for CH_2 as unity.

H_2.	O_2.	N_2.	Cl_2.	CH_4.	C_2H_4.	H_2S.	C_2H_2.	$CHCl_3$.	CS_2.
·09	·21	·22	·38	·32	·45	·79	·75	·94	·72
C_2N_2.	HCl.	CH_3Cl.	NH_3.	CO_2.	SO_2.	N_2O.	PCl_3.	CCl_4.	$(CH_3)_2O$.
·90	·83	·79	1·06	·76	·96	·83	·88	·89	·96

We see that the ratio is small for the uncombined elements and CH_4 and C_2H_4, a result of the important fact that while the refraction-equivalent of a non-metallic element is almost the same in the uncombined state as in the combined, the dynic equivalent is much smaller in the uncombined state of an element. The meaning of this fact will be discussed later on; connected with it is the fact that the ratio for most of the typical compounds in the last table is notably less than unity. A molecule has to reach a certain degree of complexity before the summative law holds as regards its dynic equivalent; the same may be said about its heat of formation. Further comment on the connexion between dynic equivalent and heat of formation must be deferred for a little.

We can now give a formal enunciation of the law of the virial constant:—If the molecule of an organic compound is of a degree of complexity higher than that of the ordinary typical compounds, then the virial constant for one gramme of the compound is given in terms of the megamegadyne, gramme, and centimetre as units by the relation

$$M^2 l = 6\,S + \cdot 66\,S^2,$$

where M is the usual molecular weight of the compound, and S is the sum of the dynic equivalents of the atoms in its molecule (measured in terms of that for CH_2 as unity).

According to the law of force $3\,Am^2/r^4$, Am^2 is proportional to $M^2 l$ and therefore follows the same law.

13. *Return to the Discontinuity during Liquefaction of Compounds and proof that it is due to the pairing of Molecules.*—The interpretation of the form of the internal virial expression above the volume k is of the highest importance in the theory of molecular force, and can now be attempted in the light of the law for $M^2 l$. If the molecules of a substance do pair to produce an actual chemical polymer of it, then its molecular mass changes from M to 2M, while S the dynic equivalent changes to 2S, and consequently

$$l \text{ or } (6\,S + \cdot 66\,S^2)/M^2$$

changes to a value given by

$$l' = (6\,S/2 + \cdot 66\,S^2)/M^2.$$

When S is small we see that the pairing of molecules to produce a polymer causes the virial constant (for one gramme) to diminish to nearly the half of its value for free molecules; when S is larger this statement becomes less exact. In the

case of CO_2, for example, if from Table XXV. we take S as 1·05, then

$$l = \cdot 00367 \quad \text{and} \quad l' = \cdot 00206,$$

but in the case of ethyl oxide, with S = 4·5,

$$l = \cdot 00738 \quad \text{and} \quad l' = \cdot 00491.$$

In both cases we see that the pairing of the molecules to form a new chemical compound or polymer is attended with a reduction of the virial constant towards one half, but not exactly to one half of the original value. Now the data given in Tables I. and III. and the form of virial term taken to represent them, $l/(v+k)$, along with the fact that below volume k the form is $l/2v$, mean that in the limiting gaseous state the virial term is practically l/v, just as below k it is $l/2v$; hence we must regard the pairing of the molecules to be such as to cause the virial constant to become one half of its higher limit—in other words, the pairing must be different from polymerization. We are therefore led to differentiate the chemical and physical pairing of molecules by the statement that while chemical pairing alters the virial constant in the ratio

$$(6\,S + \cdot 66\,S^2)/(12\,S + 2\cdot 64\,S^2) \quad \text{or} \quad (1 + \cdot 11\,S)/(2 + \cdot 44\,S),$$

physical pairing alters it in the ratio

$$6\,S/12\,S \quad \text{or} \quad 1/2.$$

The term $\cdot 66\,S^2$ would thus appear to have a certain chemical significance.

And now as to the form $l/(v+k)$ connecting the two extreme cases. We can explain it in the following manner :—It will be shown when we come to treat of solutions that if a salt having a parameter of molecular force 3 A (proportional to its virial constant l) is dissolved in a solvent with parameter 3 W so that there are n molecules of salt to one of solvent, then the solution behaves as if it consisted of molecules having a parameter 3 X given by the singular relation

$$X^{-1} = (W^{-1} + nA^{-1})/(1+n).$$

Now, in a gas being compressed towards the volume k, let us assume that there are a number of pairs of molecules proportional to k and a number of single molecules proportional to $v-k$, and that the same relation applies to the mixture of paired and single molecules as to the solvent and salt in a solution, then, replacing W by l and A by $l/2$ and n by

$k/(v-k)$, we get for the reciprocal of the virial constant of the mixture

$$X^{-1}=\left(\frac{1}{l}+\frac{k}{v-k}\cdot\frac{2}{l}\right)\Big/\left(1+\frac{k}{v-k}\right)=\frac{1}{l}\cdot\frac{v+k}{v};$$

$$\therefore\ X=lv/(v+k),$$

and therefore the virial term is $l/(v+k)$.

This would be no demonstration of the pairing of molecules in compounds, if we did not already have it proved in the case of the elements that the virial term varies inversely as the volume at all volumes. Remembering this we can accept our form $l/(v+k)$ as indicating the existence of a mixture of paired and single molecules, the number of pairs at volume v being to the number of single molecules as k to $v-k$.

The form of the energy term,

$$RT\left(1+\frac{2k}{v+k}\right),$$

must also be partly determined by this existence of pairs, but it would be foreign to our immediate subject to attempt to investigate it.

14. *Brief Discussion of the Constitution of the Alcohols as Liquids.*—To learn a little more on the subject of pairing, it will be of some profit to consider briefly here the alcohols and water, which so far have been left aside, after having been proved in Table XII. to follow in the supracritical region a different law from the usual one. But also in the liquid state the alcohols and water, while conforming to the general liquid laws in many respects, are still exceptional in others. Thus Eötvös (Wied. *Ann.* xxvii.) has shown that the alcohols will conform to his generalization if at the lower range of temperature, from 20° C. to 170° C., the molecules be considered complex (double relatively to ordinary liquids) and water also conforms if from 100° upwards its molecules be considered double; the molecular lowering of the freezing-point of water produced by the solution of bodies in it as measured by Raoult and compared with the molecular lowering for other liquids proves that relatively to these the molecule of water is double. Taking all the facts into consideration, it seems to me that the alcohols and water may be assumed, in the liquid state, to have the pairs of molecules again paired, the second pairing, however, not being of so intimate a nature

as the first, consisting of a mere approximation of the first pairs without any change in the values of A or of l.

According to this assumption we should expect the behaviour of the liquid alcohols to be represented by a form similar to our infracritical equation, and we will assume

$$pv = \mathrm{R''T}\left(1 + \frac{\sqrt{\mathrm{T}}}{\mathrm{B}} \cdot \frac{k' - v}{v - \beta}\right) - \frac{l}{2v},$$

where R″ is about 2R.

It was on the infracritical equation that our second method of finding $\mathrm{M}^2 l$ was founded, giving the relation

$$l = \frac{4}{3}\left(v_0 \frac{a}{\mu} + \frac{25}{26}\,\mathrm{R}\right) v\mathrm{T},$$

which can be applied to Amagat's data (*Ann. de Chim. et de Phys.* sér. 5, t. xi.), and Pagliani and Palazzo's (Wied. *Beibl.* ix.) for the alcohols.

Again, our assumption enables us to apply the fifth or capillarity method of finding $\mathrm{M}^2 l$ to the alcohols, if only we remember that the molecular domain becomes twice as large and its radius $2^{\frac{1}{3}}$ as large as it would be with only one pairing; hence the equation for the fifth method becomes for the alcohols

$$l = c\,\alpha\, v^{\frac{5}{3}}/(2m)^{\frac{1}{3}}.$$

Schiff's data are available.

As the latent heat and critical temperature are largely dependent on the supracritical equation, we ought not to expect the formulæ for $\mathrm{M}^2 l$ furnished by the third or latent-heat method and by the fourth or critical-temperature method to apply to the alcohols. But as the relation

$$\mathrm{M}\lambda = 19{\cdot}4\mathrm{T}_b,$$

or, empirically,

$$\mathrm{M}\lambda = 21\,\mathrm{T}_b,$$

which was deduced in the discussion of the third method, does apply approximately to the alcohols, the constant being 26, we may as well, for purposes of comparison, see what the formulæ of the third and fourth methods give in the case of the alcohols.

TABLE XXX.—M^2l for the Alcohols.

Method	Second.	Third.	Fourth.	Fifth.
Methyl	8	22 (11)	17 (9)	9·4
Ethyl.....	14	38 (19)	25 (17)	17·6
Propyl	24	.....	34 (26)	27·8
Isopropyl	24	.....	33 (25)	27·6
Isobutyl.....	34	.....	46 (38)	37·8
Isoamyl.....	47	82 (41)	57 (49)	48·1
Cetyl	.....	326 (163)		
Water	.....	11 (5·5)	9	6

The second and fifth methods give results in substantial agreement with one another; the third gives numbers which, when halved as in the brackets, come into agreement with the others; while if 8 be subtracted from the numbers furnished by the fourth method as in the brackets, the resulting numbers are in very close agreement with those given by the fifth method. That the two discrepant columns should be capable of harmonization with the two others by the simple operations of halving and of subtracting a constant is significant of some really simple principle on which the abnormality of the alcohols in the supracritical region depends.

But too much importance must not be attached to the general agreement among the numbers, as they are all founded on tentative assumptions; they simply prove that our idea of a second loose pairing of molecular pairs in the liquid alcohols is not discordant with facts.

The following are the dynic equivalents corresponding to the values of M^2l found by the fifth method compared with those calculated from the dynic equivalents of the elements and placed in the third row.

Alcohols	Methyl.	Ethyl.	Propyl.	Butyl(iso).	Amyl(iso).
Dynic equiv. found	1·35	2·35	3·4	4·3	5·1
„ „ calcul.	1·8	2·8	3·8	4·7	5·7

For water the dynic equivalent found is ·91, while 1·03 is the calculated value. The values found for the alcohols are about ·5 smaller than those calculated. If from the capillarity data we had calculated the values of M^2l and the dynic equivalent as if the alcohols were not exceptional in any way, we should have got:—

Alcohols	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.
M^2l	11·8	22·2	35	47·6	60·6
Dynic equivalent	1·65	2·8	3·9	5·1	6·1

These values of the dynic equivalents agree well with the calculated ones above, but then the values of M^2l being all increased in the ratio of $2^{\frac{1}{3}}$ to 1 are no longer in agreement with the values got by the second method.

Accordingly we see that the alcohols will require an exhaustive study for themselves, if the interesting features of their molecular structure are to be thoroughly made out. I have merely sketched lines on which their abnormality may be hopefully investigated. Those bodies, such as nitric peroxide, studied by the brothers Natanson, and acetic acid, studied by Ramsay and Young, which have been proved to have double molecules split up both by the action of heat and reduction of pressure have not been touched on in this paper; they also would require a special investigation in which our characteristic equations would lend an assistance much required.

15. *Methods of finding the Virial Constant for Inorganic Compounds, including a theory of the Capillarity and Compressibility of Solutions.*—So far I have secured only two methods of finding the virial constants and dynic equivalents of inorganic compounds from existing data, and only one of these is practically useful, namely the first, in which the surface-tensions of solutions are the source of the values; the second is based on the compressibility of solutions. Using our expression for surface-tension in terms of molecular force,

$$\alpha = \pi\bar{\rho}^2 Ae/(2+\sqrt{2}),$$

in the form

$$\alpha = A\rho^{\frac{5}{3}} m^{\frac{1}{3}}/c,$$

where c is a constant, I was led to imagine that it could be adapted to the case of a solution by means of the following suppositions:—First, that in a solution containing n molecules of dissolved substance of molecular mass p to one of solvent of molecular mass w, the solution may be assumed to be a substance of molecular mass

$$m = (w+np)/(1+n);$$

second, that if 3W is the parameter of molecular force for the solvent and 3A for the dissolved substance, then the parameter 3X for the solution is connected with W and A by the relation

$$X^{-1} = (W^{-1}+nA^{-1})/(1+n).$$

This seems highly arbitrary, but will be completely verified by the results to which it leads. I could make no progress

in the handling of solutions until, in the course of some work on the elasticity of alloys, I discovered a relation similar to the above to hold, and this proved to be the immediate clue to the treatment of solutions.

Let α_w be the surface-tension of water, then we have the following equations giving A :—

$$\alpha = X\rho^{\frac{5}{3}}\left(\frac{w+np}{1+n}\right)^{\frac{1}{3}}/c, \qquad \alpha_w = Ww^{\frac{1}{3}}/c,$$

$$A^{-1} = X^{-1} + (X^{-1} - W^{-1})/n.$$

These equations ought to give the same values of A^{-1} whatever the strength of the solution may be ; and herein lies a first test of the truth of the principles involved.

The following values of cA^{-1} for NaCl are calculated from Volkmann's data (Wied. *Ann.* xvii.) for its solution in water at 20° ; w is taken as 18, although we consider the water molecule to be complex, but this does not affect the purely relative comparison being made :—

n . . .	·105	·084	·052	·035	·017
cA^{-1} . .	1·34	1·38	1·47	1·46	1·42

Considering that the solutions range from saturation down to considerable dilution, the approach to constancy is satisfactory; but it will be noticed that, on the whole, there is a tendency for the value of cA^{-1} to increase with diminishing concentration, and this same phenomenon is to be seen in the case of almost all Volkmann's solutions, most pronouncedly in that of $CaCl_2$:—

n . . .	·091	·068	·041	·021	·011
cA^{-1} . .	2·41	2·53	2·77	2·95	3·12

This case shows us that there is a certain amount of incompleteness in our theory of the capillarity of solutions, as indeed we ought to be surprised if there were not, when we try to apply our arbitrary definition of the molecular mass of a solution to one which contains 56 parts by weight of $CaCl_2$ to 100 of H_2O as the solution for which $n = ·091$ does, and also when we assume that the concentration in the surface-layer is the same as in the body-fluid at all strengths up to saturation. If our object were an exhaustive representation of the connexion between the surface-tension of a solution and its concentration, it would be easy to introduce a slight empirical alteration into the above equations to make them exhaustive. For instance,

we might imagine that the effective value of W in a solution experiences a small change proportional to the concentration; but the equations as they stand will prove to be sufficient for our purpose if, in comparing solutions of different substances, we calculate cA^{-1} for the same value of n throughout.

In all subsequent calculations $n=18/1000$. The experimental data for surface-tensions of solutions are abundant, the chief that I know of and have used being those of Valson (*Compt. Rend.* lxx., lxxiv.), Volkmann (Wied. *Ann.* xvii.), Röntgen and Schneider (Wied. *Ann.* xxix.), and Traube (*Journ. für Chem.* cxxxix.).

The following Table contains the values of cA^{-1} for a certain number of compounds, the surface-tension being measured in grammes weight per linear metre and the half molecules of the salts of the bibasic acids being regarded as molecules.

TABLE XXXI.—Values of cA^{-1}.

	I.	Br.	Cl.	NO_3.	OH.	$\frac{1}{2}SO_4$.	$\frac{1}{2}CO_3$.
Li	4·15	2·46	·83	1·61	·83	1·61	
NH_4	3·99	2·21	·70	1·54	...	1·45	
Na	4·74	3·06	1·45	2·30	1·37	2·30	1·95
K	4·99	3·31	1·78	2·55	1·71	2·72	2·21

The study of this table brings out the fact that the differences of the numbers in any two rows or in any two columns are constant: thus the differences for the iodide and chloride of the four bases are in order 3·32, 3·29, 3·29, and 3·21, while the differences of cA^{-1} for the Na and Li salts of the monobasic acids are in order ·59, ·60, ·62, ·69, and ·54. Accordingly each atom contributes a certain definite part to the value of cA^{-1} for the molecule in which it occurs, and that part is independent of the other atoms in the molecule. I shall call this part the parameter-reciprocal modulus of the atom; we have not at present sufficient data to get its absolute value in any case, but if we make Li our standard positive radical, and Cl the standard negative, we can calculate the average values of the difference between the parameter-reciprocal modulus of a radical and its standard,—thus in the case of iodine this difference is 3·28, and in the case of Na ·61, and so on.

Before tabulating these mean values I will give the values calculated for the salts of some other metals with the values for the same salts of Li subtracted.

TABLE XXXII.

	I.	Br.	Cl.	NO_3.	$\frac{1}{2}SO_4$.
$\frac{1}{2}$Mg—Li.....	...	...	·39	·35	·53
$\frac{1}{2}$Ca—Li.....	·44	·73	·67	·55	...
$\frac{1}{2}$Sr—Li.....	...	...	1·67	1·71	...
$\frac{1}{2}$Ba—Li.....	...	...	2·49	2·52	...
$\frac{1}{2}$Zn—Li.....	...	...	1·35	...	1·33
$\frac{1}{2}$Cd—Li.....	2·24	2·42	2·15	...	2·29
$\frac{1}{2}$Mn—Li.....	...	...	1·17	·93	1·22

To these we may add the following values, obtained from the sulphates $\frac{1}{2}$Fe—Li 1·27, $\frac{1}{2}$Ni—Li 1·19, $\frac{1}{2}$Co—Li 1·15, $\frac{1}{2}$Cu—Li 1·49, $\frac{1}{3}$Al—Li ·6, $\frac{1}{3}Fe_{ic}$—Li ·5, and $\frac{1}{3}Cr_{ic}$—Li 1·0; and the two following from the nitrates Ag—Li 3·91, and $\frac{1}{2}$Pb—Li 4·51.

The following Table contains the values of the parameter-reciprocal moduluses of the different metals minus that for Li and of the negative radicals minus that for Cl.

TABLE XXXIII.

Mean Values of Parameter-reciprocal Modulus for the Metals with that for Li subtracted.

Na.	K.	NH.	$\frac{1}{2}$Mg.	$\frac{1}{2}$Ca.	$\frac{1}{2}$Sr.	$\frac{1}{2}$Ba.	$\frac{1}{2}$Zn.	$\frac{1}{2}$Cd.	$\frac{1}{2}$Mn.
·61	·90	—·15	·42	·65	1·7	2·5	1·33	2·3	1·2

$\frac{1}{2}Fe_{ous}$.	$\frac{1}{2}$Ni.	$\frac{1}{2}$Co.	$\frac{1}{2}$Cu.	Ag.	$\frac{1}{2}$Pb.	$\frac{1}{3}$Al.	$\frac{1}{3}Fe_{ic}$.	$\frac{1}{3}Cr_{ic}$.
1·27	1·2	1·15	1·5	3·9	4·5	·6	·5	1·0

The same for negative radicals with that for Cl subtracted:—

I.	Br.	NO_3.	OH.	$\frac{1}{2}SO_4$.	$\frac{1}{2}CO_3$.
3·28	1·56	·81	·04	·86	·46

It may be worth mentioning that these differences show a pretty close parallelism to the corresponding differences of the atomic refraction given by Gladstone (Phil. Trans. 1870) but not close enough to be worth dwelling on.

In the case of the organic bodies studied there was nothing analogous to this singular property possessed by these inorganic compounds of having the reciprocal of the parameter A of molecular force separable into a constant and definite parts

contributed by each constituent of the molecule. Thus we have characteristic of inorganic bodies in solution another of those properties called by Valson modular, who discovered that the density, capillary elevation, and refraction of normal solutions (gramme-equivalent dissolved in a litre of water) could all be obtained from the values for a standard solution such as that of LiCl by the addition of certain numbers or moduluses representing invariable differences for the metals and Li and for the negative radicals and Cl. Other properties of solutions have since been proved to be modular, as for instance their heats of formation from their elements and their electric conductivities. I think the modular nature of some of these properties of solutions is the outcome of this modular property in the parameter reciprocal of molecular force along with the additive property in mass. To prove this in the case of density would require a special investigation, but if we assume the property for density we can easily deduce Valson's result that the property applies to capillary elevation. Let h be the height to which a normal solution of any salt RQ rises in a tube of radius 1 millim., then

$$h=2\alpha/\rho=2\mathrm{X}\rho^{\frac{2}{3}}\left(\frac{w+np}{1+n}\right)^{\frac{1}{3}}\Big/c.$$

Let r and q be the density moduluses of the radicals R and Q, being small fractions, then $\rho=d+r+q$ where d is a constant nearly 1; also

$$\mathrm{X}^{-1}=(\mathrm{W}^{-1}+n\mathrm{A}^{-1})/(1+n),$$

so that

$$h=2\left(\frac{1+n}{\mathrm{W}^{-1}+n\mathrm{A}^{-1}}\right)(d+r+q)^{\frac{2}{3}}\left(\frac{w+np}{1+n}\right)^{\frac{1}{3}}\Big/c.$$

Remembering that in the case of a normal solution n is small, being 18/1000, we can develop the last expression in powers of n as far as the first; and it is evident that as p the molecular mass possesses the additive property and A^{-1} possesses the modular property, then h must also possess the modular property, which is Valson's result.

16. *Second method of finding the virial constant for inorganic bodies or solid bodies in general from the properties of their solutions.*—In this method the compressibility of solutions is used. If a solution could be treated as an ordinary liquid we might attempt to apply the equation of our second method for liquids, namely,

$$l=\frac{4}{3}\left(v_0\frac{a}{\mu}+\frac{25}{26}\mathrm{R}v\mathrm{T}\right.;$$

but as the solutions to be dealt with are all aqueous, and as *a*

for water at ordinary temperatures is quite abnormal, it would be useless to attempt to apply this equation to them; but from the "dimensions" of the physical quantities involved in it we may make it yield a correct form of empirical equation for solutions. If we neglect the small term 25R/26, and also the difference between v and v_0 at ordinary temperatures, the equation above suggests the simple form l varies as $1/\mu\rho^2$, that is X^{-1} varies as $\mu\rho^2$, say $KX^{-1}=\mu\rho^2$, where K is a constant, and for water $KW^{-1}=\mu_w$ the compressibility of water, and as before we have $X^{-1}=(W^{-1}+nA^{-1})/(1+n)$. But on account of the rapid alteration of the compressibility of water with pressure, and its anomalous variation with temperature, we must be prepared to admit that the part of the compressibility of a solution due to the water in it is altered from its value in pure water, and is more altered the more the water is compressed in the process of dissolving the salt. Let this compression be measured roughly by the total amount of shrinkage that ensues when 1 molecule of salt is dissolved in 1000 grms. of water, call the shrinkage Δ, and let us amend the equation given above to $KX^{-1}=\mu\rho^2+f(\Delta)$. Let suffixes a and b attached to symbols refer them to two different bodies, then

$$KX_a^{-1}-KX_b^{-1}=\mu_a\rho_a^2-\mu_b\rho_b^2+f(\Delta_a)-f(\Delta_b),$$

but

$$KX_a^{-1}-KX_b^{-1}=Kn(A_a^{-1}-A_b^{-1})/(1+n),$$

$$\therefore\ Kn(A_a^{-1}-A_b^{-1})/(1+n)=\mu_a\rho_a^2-\mu_b\rho_b^2+f(\Delta_a)-f(\Delta_b).$$

Hence selecting pairs of bodies for which $\Delta_a=\Delta_b$ approximately, we ought to get $\mu_a\rho_a^2-\mu_b\rho_b^2$ proportional to $cA_a^{-1}-cA_b^{-1}$, the values of the last expression being obtainable from Table XXXI.

To facilitate the comparison I furnish the following broad statements about Δ founded on the study of data as to the molecular volumes of salts, both solid and in solution, given by Favre and Valson (*Comp. Rend.* lxxvii.) Long (Wied. *Ann.* ix.), and Nicol (Phil. Mag. xvi. and xviii.). The modular property applies approximately to shrinkage on solution; the shrinkage of a gramme molecule of LiCl is 2, and the shrinkage for a gramme molecule is increased when for Li is substituted

	K.	Na.	NH_4.	½Ca.	½Sr.	½Ba.
by	8	7	−5	10	11	12;

and when for Cl is substituted

	Br.	I.	NO_3.	⅓SO_4.	⅓CO_3.
by	0	0	0	8	14.

After giving the values of $\mu\rho^2$ in the next table we can proceed with the comparison.

TABLE XXXIV.—Values of $10^7\mu\rho^2$.

	Cl.	Br.	I.	NO_3.	$\frac{1}{2}SO_4$.	$\frac{1}{2}CO_3$.
Li	432	484	541	457	433	
Na	441	496	550	468	444	428
K	454	507	557	480	450	437
NH_4	443	493	544	466	442	
$\frac{1}{2}$Ca	464					
$\frac{1}{2}$Sr	497					
$\frac{1}{2}$Ba	521					

The experimental data used are those of Röntgen and Schneider (Wied. *Ann.* xxix.), and those of M. Schumann (Wied. *Ann.* xxxi.) for $CaCl_2$, $SrCl_2$, and $BaCl_2$, in the case of which I calculated the compressibility for the half-gramme molecule according to his result that $\mu-\mu_w=cp$ where p is percentage of salt, using a value of c got from the more concentrated solutions.

An inspection of this table shows that $10^7\mu\rho^2$ possesses the modular property; it gives for instance the following differences for Na and Li, 9, 12, 9, 11, 11, with a mean value 10, and so on for the other metals; the mean values for the metals minus that for Li are:—

Na.	K.	NH_4.	$\frac{1}{2}$Ca.	$\frac{1}{2}$Sr.	$\frac{1}{2}$Ba.
10	20	8	32	65	89;

and for the negative radicals minus that for Cl:—

Br.	I.	NO_3.	$\frac{1}{2}SO_4$.	$\frac{1}{2}CO_3$.
52	105	25	0	−15.

We can now select pairs of bodies for which $\Delta_a=\Delta_b$ and test if $\mu_a\rho_a^2-\mu_b\rho_b^2$ is proportional to $cA_a^{-1}-cA_b^{-1}$.

The following are pairs of elements characterized by nearly equal shrinkage on solution with the values of the differences of $10^7\mu\rho^2$ and of cA^{-1} and also their ratio.

TABLE XXXV.

Equal shrinkage pair...	K, Na.	$\frac{1}{2}$Sr, $\frac{1}{2}$Ca.	$\frac{1}{2}$Ba, $\frac{1}{2}$Ca.	Br, Cl.	I, Cl.	NO_3, Cl.
Mean diff. of $10^7\mu\rho^2$...	10	33	57	52	105	25
Mean diff. of cA^{-1}...	·29	1·05	1·85	1·56	3·28	·81
Ratio of differences ...	34	31	31	33	32	31

The agreement here is excellent, as will be seen more clearly if we compare bodies not having equal shrinkage, as K and Li, for which we get the $10^7\mu\rho^2$ difference 20, the $c\mathrm{A}^{-1}$ difference ·90 with a ratio 22, or K and NH_4, for which the two differences are 12 and 1·05 with a ratio 11.

The agreement above is a verification of the theory of the compressibility of solutions, here barely outlined, and the equation

$$10^7(\mu_a\rho_a^2-\mu_b\rho_b^2)=32(c\mathrm{A}_a^{-1}-c\mathrm{A}_b^{-1})$$

when $\Delta_a=\Delta_b$ nearly constitutes a second method of getting values of $c\mathrm{A}^{-1}$; but we will not use it, as it adds no bodies to our list. It suffices to have partly verified the principles on which the first method is founded by their application to quite another physical phenomenon, and especially the principle involved in the remarkable equation

$$\mathrm{X}^{-1}=(\mathrm{W}^{-1}+n\mathrm{A}^{-1})/(1+n).$$

With the values in Table XXXIII. and that for LiCl, namely, ·83, we can obtain the value of $c\mathrm{A}^{-1}$ for any salt whose constituents are to be found in the table, or we can if we like use the actual values in Tables XXX. and XXXI.; we can then calculate $\mathrm{M}^2/c\mathrm{A}^{-1}$, which is proportional to M^2l, or $\mathrm{M}^2l=\mathrm{CM}^2/c\mathrm{A}^{-1}$, where C is a constant. To connect the values of M^2l thus found with those previously given absolutely in Table XXV., we must find the value of C/c, which we can proceed to do in the following manner :—

We have seen (Section 14) that we had better regard the molecule of water as doubled relatively to that of ordinary liquids, and as we have shown that the molecules are paired in ordinary liquids the molecules are doubly paired in water; but it was suggested that the second pairing of the pairs was not attended with any alteration in the parameter of molecular force, and that the only effect of the second pairing was to make the radius of the molecular domain of water $2^{\frac{1}{3}}$ as large as if water were an ordinary liquid. And, again, in the case of solutions the surface-tensions have been measured at about 15° C, whereas for comparison with our previous work they ought to have been measured at $2\mathrm{T}_c/3$, which for water is about 150° C. At this temperature the value of the surface-tension of water reduces, according to Eötvös, to about ·6 of its value at 15° C. Hence the equation, which treating water as an ordinary liquid and at 15° we wrote $\alpha_w=\mathrm{W}w^{\frac{1}{3}}/c$, ought for double pairing and at 150° to become $\cdot 6\alpha_w=\mathrm{W}2^{\frac{1}{3}}w^{\frac{1}{3}}/c$, and similar statements hold for the equation for α; so that values

of W, X, and A, as deduced from measurements at 15°, ought to be reduced by the factor $\cdot 6/2^{\frac{1}{3}}$, or 1/2, to give the desired values. Now in the case of homogeneous liquids in the equation $l = c\alpha v^{\frac{5}{3}}/m^{\frac{1}{3}}$ giving l in terms of the megadyne we found a value 5930 for $c/2$, with the megamegadyne as unit of force $c/2 = \cdot 00593$; and we can use this same value in the case of solutions after we have halved our values of A, or doubled those of $c\mathrm{A}^{-1}$ so far given; hence using the values of $c\mathrm{A}^{-1}$ so far given we get $\mathrm{M}^2 l = \cdot 00593\mathrm{M}^2/c\mathrm{A}^{-1}$.

Fortunately, a test of this argument is made possible by means of Traube's data for the surface-tension of solutions of certain organic acids and sugars, for which the values of $\cdot 00593\mathrm{M}^2/c\mathrm{A}^{-1}$ are given in the following Table, as well as values of S found by the relation $\mathrm{M}^2 l = 6\mathrm{S}$ (the term $\cdot 66\mathrm{S}^2$ being omitted), and also values of S calculated from the dynic equivalents in Table XXVI.

TABLE XXXVI.

	Oxalic Acid. $(COOH)_2$.	Citric Acid. $C_3H_4OH(COOH)_3$.	Glycerine. $C_3H_5(OH)_3$.	Mannite. $C_6H_8(OH)_6$.
$\mathrm{M}^2 l$	19·4	43·5	33·5	63·0
$\mathrm{S} = \mathrm{M}^2 l/6$	3·2	7·2	5·6	10·5
S from dynic equiv.	4·2	9·7	5·0	10·0

	Tartaric Acid. $C_2H_2(OH)_2(COOH)_2$.	Dextrose. $C_6H_{12}O_6$.	Saccharose. $C_{12}H_{22}O_{11}$.
$\mathrm{M}^2 l$	38·9	72·1	112·5
$\mathrm{S} = \mathrm{M}^2 l/6$	6·5	12·0	18·8
S from dynic equivalents	7·4	9·6	18·1

The agreement between the two sets of numbers is not all that could be desired, but it is good enough to show that the only part of $\mathrm{M}^2 l$ effective in a solution is the linear term in $\mathrm{M}^2 l = 6\mathrm{S} + \cdot 66\mathrm{S}^2$; and we have already seen that when the molecules of ordinary liquids pair during liquefaction the term $\cdot 66\mathrm{S}^2$ is inoperative in the process, so that there is a certain resemblance in the relations of two paired molecules and those of solvent to those of substance dissolved.

Returning to the inorganic compounds we can now tabulate the absolute values of $\mathrm{M}^2 l$, calculated according to the relation $\mathrm{M}^2 l = \cdot 00593\mathrm{M}^2/c\mathrm{A}^{-1}$. The manner of calculation is best illustrated by an example, say for KBr; first ·83 is taken as the value for LiCl, and to it are added ·90 and 1·56, taken from Table XXXIII., as the differences for K and Li and for

Br and Cl; the square of the molecular weight of KBr is divided by this sum and multiplied by ·00593 to give the tabulated value of M^2l in terms of the megamegadyne. From the value of M^2l thus found the dynic equivalent S is calculated by the relation $M^2l = 6S$, which has been seen to be appropriate to values of M^2l obtained from solutions.

TABLE XXXVII.—Values of M^2l and S.

	Cl.		Br.		I.		NO_3.		$\frac{1}{2}SO_4$.		$\frac{1}{2}CO_3$.	
	M^2l.	S.	M^2l.	S.	M^2l.	S.	M^2l.	S.	M^2l.	S.	M^2l.	S.
Li ...	12·5	2·1	18·7	3·1	25·7	4·3	17·1	2·8	10·6	1·8		
Na ...	13·7	2·3	20·8	3·5	28·0	4·7	18·8	3·1	12·8	2·1	8·6	1·4
K ...	18·5	3·1	28·3	4·7	32·4	5·4	23·5	3·9	17·2	2·9	12·8	2·1
NH_4	23·0	3·8	27·0	4·5	31·0	5·2	25·0	4·2	17·0	2·8		
$\frac{1}{2}$Mg	10·4	1·7	17·7	3·0	25·1	4·2	15·6	2·6	10·1	1·7		
$\frac{1}{2}$Ca...	12·0	2·0	19·4	3·2	26·7	4·5	17·3	2·9				
$\frac{1}{2}$Sr ...	14·2	2·4	21·8	3·6	29·3	4·9	19·5	3·2				
$\frac{1}{2}$Ba...	18·8	3·1	26·4	4·4	33·9	5·6	24·0	4·0				
$\frac{1}{2}$Zn...	12·5	2·1	...	...	...	...	...	...	12·6	2·1		
$\frac{1}{2}$Cd...	15·7	2·6	23·2	3·9	30·5	5·1	21·0	3·5	16·2	2·7		
$\frac{1}{2}$Mn	11·5	1·9	...	...	...	...	16·8	2·8	11·7	2·0		

To these may be added the following :—

	$AgNO_3$.	$\frac{1}{2}Pb(NO_3)_2$.	$\frac{1}{2}CuSO_4$.	$\frac{1}{2}FeSO_4$.	$\frac{1}{2}NiSO_4$.
M^2l.....	30·6	26·3	11·5	11·4	12·3
S.....	5·1	4·4	1·9	1·9	2·0

	$\frac{1}{2}CoSO_4$.	$\frac{1}{6}Al_2(SO_4)_3$.	$\frac{1}{6}Fe_2(SO_4)_3$.	$\frac{1}{6}Cr_2(SO_4)_3$.
M^2l.....	12·7	8·9	12·6	9·6
S.....	2·1	1·5	2·1	1·6

The additive principle holds amongst both sets of numbers except in the case of NH_4; see for instance the following list of the differences of S for the iodides and chlorides :—2·2, 2·4, 2·3, 2·5, 2·5, 2·5, 2·5, 2·5. Now we have already seen that the modular principle applies to cA^{-1} (the modular principle applies when a quantity is given by the addition of moduluses to a constant, the additive principle is a special case of the modular in which the constant is zero); the additive principle applies to M the molecular weight: hence it would appear

to be a mathematical impossibility that the modular or additive principle should apply also to M^2/cA^{-1}, rigorously; or, more accurately, if the modular principle applies rigorously to one of the quantities cA^{-1} and M^2/cA^{-1} it cannot apply rigorously to the other: but practically we find such relations amongst the numbers that both are approximately obedient to the modular principle. The case of NH_4 casts some light on the question, for with it cA^{-1} shows the same differences in the values of the chloride, bromide, iodide, and nitrate as with the other positive radicals, while M^2/cA^{-1} does not do so: this case would make it appear that the modular principle applies rigorously to cA^{-1}, but not so rigorously to M^2/cA^{-1}.

But leaving out of the count this case of NH_4, significant as it is, we can find mean values for the differences of the dynic equivalents of all the metals and Li, and of all the negative radicals and Cl; if we can obtain the absolute value of the dynic equivalent of Li and of Cl, we shall have those for all the metals and radicals. Now from the organic compounds we have already got a value 1·3 for the dynic equivalent of Cl, and hence from the value for LiCl we could obtain that for Li. The value tabulated for LiCl is 2·1, but we can obtain a mean value fairer to all the other bodies by subtracting, for example, from the value for KI the mean difference for K and Li, and for I and Cl; in this way we arrive at a mean value 1·9 for LiCl, from which, taking the value 1·3 for Cl, we should get ·6 for Li. But the refraction-equivalents of the halogens are supposed by Gladstone to be a little larger in inorganic than organic compounds; so that in the light of our previous knowledge of a close parallelism between dynic equivalents and refraction-equivalents it might be safer to assume that the dynic equivalents of Li and Cl in LiCl are in the ratio of their refraction-equivalents in that compound, namely, 3·8 and 10·7. According to this assumption the values for Li and Cl come out ·5 and 1·4, which we will adopt as true and use in the calculation of the dynic equivalents of the elements given in the following Table. These are measured of course as before in terms of that for CH_2 as unity, and, again, for comparison there are written along with the dynic equivalents the refraction-equivalents in terms of that for CH_2 as unity, calculated from Gladstone's values (Phil. Trans. 1870).

TABLE XXXVIII.

	Li.	Na.	K.	½Mg.	½Ca.	½Sr.	½Ba.	½Zn.	½Cd.
Dynic equivalent	·5	·8	1·6	·3	·55	·9	1·7	·65	1·22
Refraction-equivalent .	·5	·63	1·06	·46	·68	·90	1·04	·67	·9

	Ag.	½Pb.	½Cu.	½Mn.	½Fe.	½Ni.	½Co.	⅓Al.	⅓Fe.
Dynic equivalent	2·70	2·0	·6	·5	·6	·7	·8	·2	·8
Refraction-equivalent .	2·06	1·63	·76	·8	·81	·69	·71	·37	·93

	⅓Cr.	Cl.	Br.	I.	NO_3.	½SO_4.	½CO_3.	½CrO_4.
Dynic equivalent	·3	1·4	2·7	3·8	2·3	1·35	·5	1·7
Refraction-equivalent .	·7	1·4	2·2	3·6	1·8	1·1	·8	2·4

Again we see a remarkable parallelism between the dynic and refraction-equivalents of the elements and radicals. Of course there are refinements which will yet have to be made in the calculation of the dynic equivalents, but it is not likely that they will make the parallelism seriously closer.

17. *Meaning of the Parallelism between Dynic and Refraction Equivalents, and general speculations as to the volumes of the atoms and their relation to ionic speeds.*—We are now called upon to consider the meaning of this parallelism which has been demonstrated both for organic and inorganic compounds, and we shall be helped thereto by the very simple theory which I have given of the Gladstone refraction-equivalent (Phil. Mag. Feb. 1889), showing that to a first approximation

$$(n-1)u = \Sigma(\mathrm{N}-1)\mathrm{U},$$

where n is the index of refraction and u the molecular domain of a substance, N the index of the matter of an atom, and U its volume in the molecule. Hence the refraction-equivalent of an element is the product of the refractivity (Sir W. Thomson's name for index minus unity) of the substance of its atom and the volume of the atom (the volume of the atom being measured in terms of the unit in which the molecular domain, usually called molecular volume, is measured); so that the re-

fraction-equivalent is a function of the two variables only, namely, the volume of the atom and the velocity of light through it. Now we have seen that the expression M^2l, as a whole, in one aspect appears to be not dependent directly on the molecular mass M, seeing that M^2l can be represented in terms of certain quantities which we have called dynic equivalents. Hence, as l is proportional to A in our expression $3Am^2/r^4$ for molecular force, we see that in one aspect molecular force seems to be not directly dependent on the mass of the attracting molecules; and yet, on the other hand, in considering solutions we found that the quantity A asserted its individuality as separate from the whole expression Am^2, so that in another aspect there does appear to be a mass action in the attraction of two molecules. However, regarding M^2l or Am^2 as a whole, the simplest hypothesis we can make about the mutual action of molecules is that it depends most on the size of the molecules. This would make Am^2 a simple function of U; so that the dynic and refraction equivalents would have this in common, that they are both simple functions of U. Suppose, now, that the velocity of light through all matter in the chemically combined state is approximately the same, or that N is approximately the same for all atoms as constituents of compound molecules, then the refraction-equivalents given by Gladstone are directly proportional to the volumes of the atoms in the combined state, and then the parallelism between dynic and refraction equivalents would mean that S is nearly proportional to the volume. It is very interesting, therefore, to inquire briefly whether there is any evidence to prove that Gladstone's refraction-equivalents are proportional to the volumes of the atoms; and I think that in Kohlrausch's velocities of the ions in electrolysis we have such evidence. If different solutions, such as those of KCl, NaCl, or $\frac{1}{2}BaCl_2$ are electrolysed under identical circumstances, then we know, according to Faraday's law, that each atom of K and of Na, and each half-atom of Ba, may be considered to receive the same charge, so that they acquire their ionic speeds under the action of the same accelerating force. Accordingly, the ionic speed characteristic of an atom is reached when the "frictional" resistance to its motion is equal to this accelerating force; hence the "frictional" resistance is the same for all atoms, or rather for all electrochemical equivalents. Now the "frictional" resistance will be a function of the velocity of the atom and of its domain (atomic volume) and of its actual volume as well as of the domain and actual volume of the molecule of the solvent; but if water is the solvent in all cases, the only quantities which vary from body

to body are the velocity and the domain and volume of the ions, so that we can say

$$\text{“frictional” resistance} = \phi(V, u, U),$$

or

$$V = F(u, U).$$

Now the simplest connexion that one can imagine between the velocity and the domain and volume of the ion is that the velocity will be greatest when the free domain or the difference between the domain and the volume is greatest, or, to be more general, when the difference between the domain and some multiple of the volume is greatest; but if N is the same for all combined atoms, then U is proportional to the refraction-equivalent q. Hence the form of F is such that it contains $u-aq$, where a is a constant. On studying the experimental data I found that a might be considered unity, and that V is a linear function of $u-q$. There is a little difficulty in determining with accuracy the domain of an ionic atom in a solution. Nicol, in his work (Phil. Mag. xvi., xviii.) on the molecular domains of inorganic compounds in solution, has confined his attention almost entirely to differences of domains, making the assumption suitable to his purpose that the molecular domain of water is unaltered in solutions, whereas we should expect that the greater part of the shrinkage occurring on solution of an inorganic crystal happens in the water, which is far more compressible than the crystal.

Accordingly I take the molecular domains of salts in the solid state, as given by Long in his paper on diffusion of solutions (Wied. *Ann.* ix.), as nearer to the true domain when they are in solution than Nicol's values; but to allow to a certain extent for the change of state on solution, I have assumed that in each case the water experiences four fifths of the total shrinkage and the dissolved salt one fifth. This is an arbitrary adjustment, and is of no material importance to the comparison to be made except as showing that the point has not been overlooked. In the following Table are given under u the molecular domains, under q the molecular refractions (Gladstone's), in the next column their differences, under k the specific molecular conductivities determined in highly dilute solution by Kohlrausch and shown by him to be equal to the sum of the velocities of the ions in each case. These are taken from his paper (Wied. *Ann.* xxvi.), with a few additions from an earlier one (Wied. *Ann.* vi.). Under k (calculated) are given values of the conductivity calculated from the equation

$$k = 68 + 2{\cdot}2\,(u-q),$$

expressing the linear relation between conductivity or sum of ionic velocities and $u-q$.

TABLE XXXIX.

	u.	q.	$u-q$.	k.	k (calc.).
KI	53·5	35·3	18	107	108
KBr	44	25	19	107	110
KCl	36	18·8	17	105	105
NaI	41	32	9	87	88
NaBr	32	21·7	10	87	90
NaCl	24	15·5	8·5	87	87
LiCl	20·5	14·5	6	78	81
$\frac{1}{2}MgCl_2$	20	14	6	80	81
$\frac{1}{2}CaCl_2$	22	16	6	81	81
$\frac{1}{2}SrCl_2$	24	17·5	6·5	83	82
$\frac{1}{2}BaCl_2$	24	18·6	5·4	86	80
$\frac{1}{2}ZnCl_2$	23	15·8	7	77	83

The agreement is here such as to prove a true connexion between conductivity and $u-q$, the more striking as no relation can be seen between conductivity and u or q taken separately. The only bodies I have omitted from Kohlrausch's latter list are the nitrates of some of the above metals and of silver, the hydrogen compounds of the halogens, and the ammonium compounds. These do not give results in harmony with those in the last table, and, indeed, we should hardly expect a compound radical like NO_3 to experience frictional resistance in the same manner as a single atom like Cl, and as to the hydrogen compounds they form a class by themselves with respect to many physical properties. It will be as well to show the amount of departure in these cases in the following Table :—

	u.	q.	$u-q$.	k.	k (calc.).
HI	56	26	30	327	134
HBr	50	16	34	327	142
HCl	42	11	31	324	136
KNO_3	47	22	25	98	123
$NaNO_3$	36	19	17	82	105
NH_4NO_3	47·5	25·5	22	98	116
NH_4Cl	35·5	22·2	13	104	97

Kohlrausch has pointed out that there is some difficulty in determining the true connexion between ionic velocities and conductivities in the case of the bibasic acids SO_4 and CO_3, so that we must leave them out of the count for the present.

18. *An Attempt to Determine the Velocity of Light through the substance of the water-molecule.*—In spite of the exceptions, the relation demonstrated in Table XXXIX. is sufficiently striking. To explain it, let us replace q by its value $(N-1)U$; then, in interpreting the expression $u-(N-1)U$ as occurring in our expression for the conductivity of a solution, there are two methods of procedure: first, we can assume that $u-U$, the free or unoccupied part of the domain, is the most likely to occur, in which case $N=2$; second, that $u-cU$ occurs in the expression for conductivity, and that c happens to have the same value as $N-1$, on which supposition it would be desirable to determine N. At present I know of only one way of attempting to find N or v/V, the ratio of the velocity of light through free æther to its velocity through the matter of an atom, namely by means of Fizeau's experiment, repeated by Michelson and Morley, on the fraction of its motion communicated by flowing water to light passing through it. Exactly in the manner of my paper (Phil. Mag. Feb. 1889, p. 148) we can estimate the effect of the motion of matter on the light passing through it. Let s be the distance travelled by light in water flowing through the æther at rest with a velocity δ in the same direction as the light, v'' the mean velocity of light through the flowing water, v' the mean velocity through still water, v its velocity through free æther, V through a molecule of water, l the mean distance through a molecule, and a its mean sectional area; then the total loss of time experienced by a wave of unit area of front or a tube of parallel rays, or, briefly, a ray of unit section in passing through the matter-strewn path s instead of a clear path in free æther, will be equal to its loss in a molecule multiplied by the number of molecules passed through in the path. This number, when the matter is at rest, is proportional to s, to a, and to ρ/M, or it varies as $sa\rho/M$; but when the matter is in motion it is reduced in the ratio $1-\delta/v'':1$. The loss of time in each molecule is found thus: l/V is the time taken to pass through a molecule, and in this time the molecule moves a distance $l\delta/V$ and the unit wave-front moves a distance $l(1+\delta/V)$, which in free æther would take a time $l(1+\delta/V)/v$; so that the loss of time in a molecule is $l/V-l(1+\delta/V)/v$. Hence, the total loss of time in the path s may be written

$$\frac{ksal\rho}{M}\left(\frac{1}{V}-\frac{1+\frac{\delta}{V}}{v}\right)\left(1-\frac{\delta}{v''}\right).$$

But the loss of time is also $s/v''-s/v$; equating the two ex-

pressions and putting $M/\rho = u$ and $al = U$, $v/v'' = n''$, $v/V = N$ we get

$$u(n''-1) = U\left(N-1-\frac{\delta}{v}N\right)\left(1-\frac{\delta}{v}n''\right):$$

as k is equal to 1, seeing that if $\delta = 0$ and $U = u$, then N must be equal to n. This equation is the companion to that for still matter, namely,

$$u(n-1) = U(N-1).$$

But to allow for deformation of the wave-front in passing through molecules it was shown (Phil. Mag. Feb. 1889, p. 150) that this first approximation might be altered to the form

$$u(n-1) = U(N-1) + c\rho,$$

where c is a constant, and this form was verified, so that we may write

$$u(n''-1) = U\left(N-1-\frac{\delta}{v}N\right)\left(1-\frac{\delta}{v}n''\right) + c\rho$$

$$= U(N-1)\left(1-\frac{\delta}{v}\cdot\frac{N}{N-1}-\frac{\delta}{v}n''\right)+c\rho,$$

neglecting the term in δ^2;

$$\therefore\ u(n''-n) = -\frac{\delta}{v}U(N-1)\left(\frac{N}{N-1}+n''\right)$$

$$\therefore\ \frac{n''-n}{n} = -\frac{\delta}{v}\frac{U(N-1)}{u(n-1)}\cdot\frac{n-1}{n}\left(\frac{N}{N-1}+n''\right).$$

Now

$$\frac{n''-n}{n} = \frac{v'-v''}{v''} = -\frac{x\delta}{v''} = -\frac{x\delta}{v'} \text{ approximately,}$$

where x is the fraction of the water's velocity imparted to the velocity v' to change it to v''. Fizeau (*Ann. de Ch. et de Phys.* sér. 3, t. lvii.) found a value ·5 for x, while Michelson and Morley (Amer. Journ. Sc. ser. 3, vol. cxxxi.), in a more extended and accurate series of experiments, found a value $x = \cdot 43 \pm \cdot 02$, which we will adopt. $U(N-1)$ is equal to $u(n-1)$ measured in the vapour of water, for which Lorenz (Wied. *Ann.* xi.) gives the value 5·6; the value for water at 20° C., according to his data is 6, and n is 1·333, which may also be taken as the value for n'' where it occurs; all these values being substituted in the equation

$$\frac{N}{N-1} = x\frac{n^2}{n-1}\cdot\frac{u(n-1)}{U(N-1)} - n''$$

give the value $N=9$. Hence the velocity of light through the water molecule appears to be one ninth of that through free æther. But before we could ascribe any degree of accuracy to this estimate we should need to be surer of the value of x, whose measurement is attended with great experimental difficulties. It is much to be desired that we had similar measurements for other bodies than water, both liquid and solid, to permit of other estimates of N, so as to see if it is the same for all compound bodies, and also to decide between the theory here sketched and Fresnel's hypothesis, that matter carries its own excess of æther with it, so that $x=(n^2-1)/n^2$, which in the case of water is ·437, in excellent agreement with Michelson and Morley's experimental number; but one such agreement is not sufficient to establish an hypothesis founded on such artificial grounds. However, if $N=9$ then $N-1=8$, and we have the electrical specific molecular conductivity $k=68+2{\cdot}2\ (u-8U)$. It is only a coincidence that this agrees so exactly in form with Clausius's calculation that the number of encounters experienced per second by a molecule of volume U moving amongst a number of others of volume U is greater than that experienced by an ideal particle moving under the same circumstances in the ratio $u:u-8U$. Further experiment must elucidate the subject-matter of these speculations.

19. *Suggested relation between the change in the volume of an atom on combination and the change in its chemical energy.*—Returning to the idea that the dynic equivalent furnishes a measure of the volume of its atom, we can get a suggestive glimpse into the relation between the volume of an atom and its chemical energy. Kundt has recently (Phil. Mag. July 1888) shown that the velocities of light through the metals (uncombined) are as their electrical conductivities, being in the case of silver, gold, and copper greater than through free æther, and as in this case both $n-1$ and $N-1$ are negative, we see that $(n-1)u$ or $(N-1)U$ for the metals changes greatly when the metals pass from the combined to the free state. Now this is in strong contrast to the behaviour of the non-metallic elements, which have been shown in the case of O, N, C, S, P, Cl, Br, and I to possess nearly the same values of $(n-1)u$ in the combined and free states, and the same may perhaps be said of H. Again, in contrast to this approximate inalterability of $(n-1)u$ for these non-metals we have the fact, already pointed out, that the dynic equivalents of H, O, and N are much smaller in the free than the combined state. If, then, the dynic equivalents give a measure of the volumes

of the atoms in both states, we must consider the volumes of free H, O, and N to be smaller than when they are combined, the change of volume corresponding to the change of energy on combination. If this is true, then the elasticity and density of the non-metallic atoms (or the equivalents of these properties in the electromagnetic or any other theory of light) are so related that although the density changes $(N-1)U$ remains constant, whereas in the metallic atoms the relation between density and elasticity must be quite different, because, as we have seen, $(N-1)U$ actually changes sign in some cases.

It would be possible to determine approximate values for the dynic equivalents of the uncombined metals from Quincke's data for the surface-tension of melted metals, and also to get some light on the constitution of salts from his measurements of the surface-tension of melted salts, but these would be most appropriately discussed in connexion with a general study of the elastic properties of solids. I have, however, satisfied myself that the dynic equivalents of the uncombined metals are different from their values in the combined state.

To show the existence of an intimate relation between dynic equivalents and chemical energy we can enumerate the following propositions:—That in the great majority of inorganic compounds the evolution of heat accompanying the passage of an atom from the uncombined to the combined state is almost independent of the nature of the atoms it combines with, similarly the change of dynic equivalent of an atom on combination is almost independent of the nature of the atom it combines with; that in organic compounds with the exception of the simpler typical forms the same proposition as this applies both as regards heat and dynic equivalent.

These general remarks are intended to indicate the most hopeful direction for the continuation of these researches to open up new fields; and yet in old fields there is abundance of scope for the application of the law of molecular force towards the acquisition of a knowledge of the structure of molecules, in the elasticity of solids, in the viscosity of gases and of liquids, in the kinetics of solutions, and many kindred subjects.

Melbourne, February 1890.

XXVIII. *The Fusion-Constants of Igneous Rock.*—Part III. *The Thermal Capacity of Igneous Rock, considered in its Bearing on the Relation of Melting-point to Pressure.* By CARL BARUS *.

[Plate VI.]

1. *INTRODUCTORY.*—The present experiments are in series with the volume-measurements of my last paper, and the same typical diabase was operated upon. Since it is my chief purpose to study the fusion behaviour of silicates, more particularly the relation of melting-point to pressure, the observations are restricted to a temperature-interval (700° to 1400°) of a few hundred degrees on both sides of the region of fusion † (§ 11).

2. *Literature.*—Experiments similar to the present, but made with basalt, were published quite recently ‡ by Profs. Roberts-Austen and Rücker §. The irregularities obtained by these gentlemen with different methods of treatment (heating in an oxidizing or a reducing atmosphere, repeated heating, sudden cooling), the anomalously large specific heat between 750° and 880°, where basalt is certainly solid, and the absence of true evidences of latent heat ‖, contrast strangely with the uniformly normal behaviour occurring throughout my own results. Basalt is chemically and lithologically so near akin to diabase (particularly after melting) that I anticipated a close physical similarity in the two cases. Unfortunately the account given of the basalt work is meagre. Detailed comparisons are therefore impossible.

The elaborate measurements of Ehrhardt (1885) and of Pionchon (1886–7) are less closely related to the present work.

APPARATUS.

3. *The Rock to be tested.*—About 30 grammes of diabase were fused in the small platinum crucible together with which they were to be dropped into the calorimeter. Two such charged crucibles were in hand, to be used alternately. The molten magma, after sudden cooling, shows a smooth, apparently unfissured surface, glossy and greenish black. After

* Communicated by the Author.

† The geological account of the present work is begun by Mr. Clarence King, in the January number of the American Journal.

‡ This was written some time ago. See American Journal, December 1891 and January 1892. A forthcoming Bulletin, No. 96, U.S. Geological Survey, contains the work in full.

§ Roberts-Austen and Rücker: this Magazine, xxxii. p. 355 (1891).

‖ Supposing basalt to solidify (§ 13) below 1200°.

drying and weighing, the mass is often found to have gained 5 per cent. in weight. I was at first inclined to believe that this was attributable to water chemically absorbed by the viscous magma; but the water is only mechanically retained, for it passes off after 24 hours of exposure to the atmosphere, or by drying at 200° C. for, say, 30 minutes. Hence I weighed my crucibles at the beginning of each measurement, having previously dried them at 200°. The solid glass, suddenly cooled from red heat, soon shows a rough and fissured surface, and its colour changes from black to brown, possibly from the oxidation of proto- to sesquisalt of iron, possibly from mere changes in the optical character of the surface (§ 2).

Throughout the course of the work the charge of the crucibles was neither changed nor replenished.

4. *Thermal Capacity of Platinum.*—Data sufficient for the computation of the heat given out by the crucibles were published in 1877 by Violle*, whose datum for the high temperature (t) specific heat of platinum is $\cdot 0317 + \cdot 000012t$. Hence the increase of thermal capacity from zero Centigrade to the same temperature is $t(\cdot 0317 + \cdot 000006t)$, which is the allowance to be made per gramme of platinum crucible.

5. *Furnace.*—Inasmuch as heat is rapidly radiated from the white-hot slag, it is necessary to transfer the crucible from the furnace into the calorimeter swiftly. I discarded trap-door, false bottom, and other arrangements for this purpose, because the mechanism clogs the furnace, interferes with constant temperature, and is too liable to get out of order. The plan adopted is shown in figs. 1 and 2 (Plate VI.), in sectional elevation and plan. The body of the furnace consists of two similar but independent bottomed half-cylinders, A A and B B, of fire-clay properly jacketed, which come apart along the vertical plane *c c c c*. The lid, L L, however, is a single piece, and fixed in position by an adjustable arm (not shown). Each of the halves of the furnace is protected by a thick coating of asbestos, C C, D D, and by a rigid case of iron, E E, F F. Set screws, *g g g g*, pass through the edges of this in such a way as to hold the fire-clay and asbestos in place. The horizontal base or plate of the casing E F is bent partially around the two iron slides, G G, along which the two halves of the furnace may therefore be moved at pleasure while the lid is stationary; as is also the blast-burner, H, clamped on the outside (not shown), and entering the furnace by a hole left for that purpose.

* Violle's calorimetric work will be found in *C. R.* lxxxv. p. 543 (1877), lxxxvii. p. 981 (1878), lxxxix. p. 702 (1879); Phil. Mag. [4] p. 318 (1877).

The charged crucible is shown at K (figs. 1, 2, and 3), and is held in position by two crutch-shaped radial arms, N, N, of fire-clay, the cylindrical shafts of which fit the iron tubes P, P, snugly, and are actuated by two screws, R, R. Moreover P, P are covered with asbestos (not shown), and thus subserve the purpose of handles, by grasping which the two halves of the furnace may be rapidly jerked apart. It is by this means that the crucible is suddenly dropped out of the furnace into the calorimeter immediately below (not shown). Care must be taken to have the arms N, N free from slag.

6. *Temperature.*—As in the former work, the temperature of the furnace is regulated by forcing the same quantity of air swiftly through it at all times, but lading this air with more or less illuminating-gas, supplied by a graduated stopcock. The amount of gas necessary in any case is determined by trial, and observations are never to be taken except after 15 or 20 minutes' waiting, when the distribution of temperature is found to be nearly stationary. Nevertheless the temperature of the crucible is never quite constant from point to point. I therefore measured this datum at three levels—near the bottom, the middle, and the top of the charge, after the stationary thermal distribution had set in (see Tables, § 10). For this purpose the fire-clay insulator*, *t t*, of the thermocouple, *a b*, passing through a hole in the lid, is adjustable along the vertical. Before dropping the crucible the thermocouple is withdrawn from the charge and suspended above it. The cold junction is submerged in petroleum and measurements made by the zero method.

When the charge is solid, a small platinum tube previously sunk axially into the mass (see fig. 3) enables the observer to make the three measurements for temperature as before. In my later work I also encased the insulator of the thermocouple in a platinum tube closed below (see fig. 1) when making these measurements for the molten charge. Slag being a good conductor at high temperatures, hydroelectric distortions of the thermoelectric data may not otherwise be absent.

I state, in conclusion, that when constancy of temperature is approached the hole in the lid is closed with asbestos, and the products of combustion escape by the narrow seam in the side of the furnace, through which, moreover, crucible and appurtenances are partially visible.

* These are cylindrical stems, 0·5 centim. thick, 25 centim. long, with two parallel canals running from end to end, through which the platinum wires are threaded. *Cf.* Bulletin U.S. Geolog. Survey, No. 54, p. 95 (1889).

7. *Calorimeter.*—A hollow cylindrical box, provided with a hollow hinged lid, through both of which a current of cold water at constant temperature continually circulated, surrounded the calorimeter on all sides. Thus the temperature of the environment was sharply given, and the correction for cooling could be found and applied with accuracy.

The calorimeter was a vessel of thin tinned sheet iron, 28 centim. long, 8 centim. in diameter, having a water-value of 19 gramme-calories, and holding a charge of about 1200 grammes of water. The inside of the vessel was provided with a fixed helical strip running nearly from top to bottom, and was supported on a hard rubber stem. This could be actuated on the outside of the outer case from below, and served as a vertical axle around which the calorimeter could be rotated. In this way the water within the vessel was churned, and three small hard rubber rowels near the top gave steadiness to the rotation. I pass the description of this apparatus rapidly here, but shall recur to it in connexion with other calorimetric work.

The box or outer vessel of the calorimeter, with its projecting stem, was movable on a small tramway, the tracks of which lay at right angles to the slides G, G (figs. 1 and 2). Thus at the proper time the lid of the box was opened and the calorimeter rolled directly under the furnace. After receiving the crucible the calorimeter was again rolled away and the box closed, whereupon the temperature-measurements were made by a sensitive thermometer inserted through a hole in the lid.

Were I to continue work like the present I should make the crucible bullet-shaped, and provided with a permanent central tube much like fig. 3. The splashing of water by the dropping crucible (an annoyance which is sometimes serious) would then be to a great extent obviated.

Results.

8. *Method of Work.*—While waiting for stationary furnace temperature I made the initial measurements for the cooling of the calorimeter in time series. Knowing, therefore, the time at which the body was dropped I also knew the temperature of the water into which it was dropped, accurately. Similarly the three measurements for the temperature of the charge had just before this been made in time series.

The experiments showed that ten minutes after submergence the crucible and charge might safely be considered cold, for the maximum temperature of the calorimeter was

reached after 5 minutes. Hence the time from 10 to 15 minutes was available for making the final measurements for cooling; knowing the extremes, I found the intermediate rates in accordance with the law of cooling. Thus, while the calorimeter was being constantly stirred, its temperature was measured at the end of each minute. Hence I knew the mean excess of its temperature above its environment during the course of every minute, and was able to add the corresponding allowance for radiation and evaporation at once. How important this correction is the Tables (§ 10) fully show. The only drawback against sharp values is the lag error of the thermometer; but this is eliminated in a long series.

I have stated that both the calorimeter and the crucible were weighed before and after each measurement. The latter data were taken.

9. *Arrangement of the Tables.*—The two crucibles (§ 3) and tubes (fig. 3) are designated I. and II. In all cases m is the mass of the charge, M the calorimetric value of the calorimeter (corrected for temperature), τ the temperature of the environment. Θ is the temperature at the top, the middle, and the bottom of the charge at the time of submergence. The mean value is also given. The temperature of the calorimeter at the time specified is given under θ, and a parallel column shows the correction of θ for radiation. Finally, the computed thermal capacity of the platinum crucible and appurtenances (correction h), and the thermal capacity* h of the charge computed up to each of the consecutive times, are found in the last columns. A few obvious remarks follow. Note that h reaches its true (constant) value in proportion as the body is cold.

To avoid prolixity I have only given full examples of the data here defined at the head of each table. The remainder is abbreviated.

10. *Tables.*—In the data of the first series (Table I.) only one value of Θ is in hand for the liquid state. Moreover the construction of the furnace was somewhat faulty, not being flat-bottomed. Hence these results are of inferior accuracy as compared with Series II. (Table II.), which are the best obtained.

* The constant h is really the increase of thermal capacity above zero degrees Centigrade.

TABLE I.—Thermal Capacity of Diabase. First Series.

Platinum crucible, I., 11·169 g.; Platinum tube, I., ·985 g.
Platinum crucible, II., 11·271 g.; Platinum tube, II., ·654 g.

Cruc. No.	τ.	Time.	Θ.	Mean Θ. M. m.	θ.	Correction θ.	Correction h.	h.	
	°C.	Minutes.	°C.		°C.	°C.	g.-cal.	g.-cal.	
I.	12	0	.....	1367°	14·92	.....	.....	.....	Immersion
		1	.....	1202 g.	22·80	·02	17·9	267	Liquid.
		2	.....	33·36 g.	25·20	·06		355	
		3			25·50	·11		367	
		5			25·58	·20		372	
		8			25·40	·33		370	370
		11			25·25	·46		370	
		14			25·12	·60		370	
I.	16	0	.....	1306°	25·90	.....	.....	.....	Immersion
		11	.....	1145 g.	36·04	1·10	16·6	364	Liquid.
			.....	33·75 g.					
II.	12	0	.....	1378°	22·16	.....	.....	.....	Immersion
		14	.....	1202 g.	30·97	1·11	20·7	385	Liquid.
			.....	29·32 g.					
I.	12	0	.....	1337°	14·55	.....	.....	.....	Immersion
		14	.....	1196 g.	24·40	·69	18·0	373	Liquid.
			.....	32·22 g.					
II.	12	0	.....	1274°	21·92	.....	.....	.....	Immersion
		14	.....	1196 g.	29·98	1·10	17·1	358	Liquid.
			.....	29·16 g.					
I.	12	0	1199	1166°	14·87	.....	.....	.....	Immersion
		14	1163	1195 g.	22·98	·81	16·7	311	Solid.
			1138	32·22 g.					
II.	12	0	1100	1078°	21·16	.....	.....	.....	Immersion
		14	1074	1196 g.	27·25	·74	16·4	263	Solid.
			1060	29·16 g.					
I.	11	0	1021	1001°	14·89	.....	.....	.....	Immersion
		11	998	1196 g.	21·31	·47	13·9	242	Solid.
			983	32·23 g.					
II.	11	0	1035	1025°	19·76	.....	.....	.....	Immersion
		14	1025	1195 g.	25·55	·73	15·5	253	Solid.
			1015	29·16 g.					
I.	11	0	889	880°	16·19	.....	.....	.....	Immersion
		11	880	1198 g.	21·59	·41	12·0	204	Solid.
			872	32·24 g.					
II.	11	0	827	829°	20·07	.....	.....	.....	Immersion
		14	827	1192 g.	24·39	·65	12·1	191	Solid.
			833	29·16 g.					

TABLE II.—Thermal Capacity of Diabase. Second Series.

Cruc. No.	τ.	Θ.	Mean Θ. M. m.	Time.	θ.	Correction θ.	Correction h.	h.	
	°C.	°C.		Minutes.	°C.	°C.	g.-cal.	g.-cal.	
II.	12	1265	1251°	0	18·94	.....	.....	.....	Immersion
		1246	1189 g.	1	24·60	·04	20·6	236	Liquid.
		1241	26·39 g.	2	26·05	·10		305	
				3	26·52	·16		329	
				5	26·61	·30		339	
				8	26·45	·50		341	340·5.
				11	26·25	·69		340	
				14	26·08	·88		341	
I.	12	997	993°	0	14·07	.....	.....	.....	Immersion
		995	1192 g.	11	20·61	·22	13·8	238·3	Solid.
		987	32·22 g.						
II.	12	1260	1251°	0	19·34	.....	.....	.....	Immersion
		1251	1190 g.	14	26·49	·80	20·8	342·5	Liquid.
		1243	26·07 g.						
II.	10	1354	1334°	0	13·78	.....	.....	.....	Immersion
		1333	1190 g.	14	21·79	·84	22·4	376·6	Liquid.
		1319	26·27 g.						
I.	10	954	948°	0	20·24	.....	.....	.....	Immersion
		948	1186 g.	14	25·81	·94	13·0	226·6	Solid.
		942	32·22 g.						
II.	10	1364	1352°	0	17·18	.....	.....	.....	Immersion
		1354	1194 g.	14	24·82	·87	23·1	367·0	Liquid.
		1339	26·05 g.						
I.	10	877	873°	0	14·83	.....	.....	.....	Immersion
		873	1191 g.	14	20·13	·46	11·9	202·1	Solid.
		870	32·20 g.						
II.	10	1176	1166°	0	17·40	.....	.....	.....	Immersion
		1164	1187 g.	14	24·21	·77	19·2	309·5	Liquid.
		1158	25·97 g.						
II.	10	1215	1197°	0	14·38	.....	.....	.....	Immersion
		1191	1192 g.	14	21·13	·62	19·9	318·5	Liquid.
		1186	25·95 g.						
I.	10	782	781°	0	19·36	.....	.....	.....	Immersion
		780	1189 g.	14	23·61	·94	10·4	179·7	Solid.
		780	32·19 g.						
II.	10	1204	1194°	0	14·54	.....	.....	.....	Immersion
		1195	1195 g.	14·5	21·22	·66	19·9	317·9	Liquid.
		1183	25·90 g.						

Table II. (*continued*).

Cruc. No.	τ.	θ.	Mean θ. M. m.	Time.	θ.	Correction θ.	Correction h.	h.	
	°C.	°C.		Minutes.	°C.	°C.	g.-cal.	g.-cal.	
I.	10	1177 1170 1166	1171° 1192 g. 32·20 g.	0 14	19·88 27·37	..... 1·10	..... 16·7	..... 301·6	Immersion Solid.
I.	11	1106 1094 1088	1096° 1195 g. 32·21 g.	0 14	16·28 23·24	..... ·68	..... 15·5	..... 268·2	Immersion Solid.
II.	11	1262 1244 1238	1248° 1191 g. 25·49 g.	0 14	19·72 26·55	..... ·89	..... 21·1	..... 338·8	Immersion Liquid.
I.	11	1237 1216 1202	1218° 1188 g. 29·43 g.	0 14	13·67 21·60	..... ·69	..... 17·7	..... 330·3	Immersion Liquid.
II.	11	1224 1216 1205	1215° 1185 g. 25·57 g.	0 14	19·73 26·27	..... ·95	..... 20·4	..... 326·6	Immersion Liquid.

For brevity the later observations were averaged per 3 minutes, and under h the mean value for the last 11 minutes is usually given.

In Series I. the increase of temperature from top to bottom of the crucible is as large as 60° at 1200°, usually much smaller, however, and falling off pretty regularly to 6° at 829°. In Series II. the corresponding mean difference is about 25° at 1300°, 14° at 1000°, 10° at 800°. The errors thus involved cannot be greater than 2 per cent. in the extreme case; but since the distribution of temperature is *measured*, it is probably negligible except at very high temperatures. I am inclined to infer that the greater constancy of the solid distribution as compared with the liquid is due to greater thermal conductivity in the former case (solid), convection being necessarily absent in both.

Considering the observational work as a whole, the data are satisfactory, seeing that an error of 0·1° C. in the calorimetric temperatures, initial or final, must distort the results at least 1 per cent. But the real source of error is probably accidental, and is encountered when the hot body falls through the surface of the cold water.

Inferences.

11. *Digest and Charts.*—In Tables III. and IV. I have summarized the chief results on a scale of temperature. The

results of the latter (Series II.) are graphically shown in the chart (fig. 4), in which thermal capacity in gramme-calories is constructed as a function of temperature *. Straight lines are drawn through the points, showing the mean specific heats for the intervals of observations, solid and liquid. The letter *a* marks the region of fusion.

TABLE III.—Thermal Capacity of Diabase. Series I. Digest, *cf.* § 15.

Mean specific heat, solid, 800° to 1100° . ·304.
" " " liquid, 1200° to 1400° . ·350.
Latent heat of fusion, at 1200°, 24 g.-cal.; at 1100°, 16 g.-cal.

Solid.				Liquid.			
Temp.	Thermal capacity.	Temp.	Thermal capacity.	Temp.	Thermal capacity.	Temp.	Thermal capacity.
°829	191	°1025	253	°1274	358	°1367	370
880	204	1078	263	1306	364	1378	385
1001	242	†1166	311	1337	373		

TABLE IV.—Thermal Capacity of Diabase. Series II. Digest, *cf.* § 15.

Mean specific heat, solid, 800° to 1100° . ·290.
" " " liquid, 1100° to 1400° . ·360.
Latent heat of fusion, at 1200°, 24 g.-cal.; at 1100°, 16 g.-cal.

Solid.				Liquid.			
Temp.	Thermal capacity.	Temp.	Thermal capacity.	Temp.	Thermal capacity.	Temp.	Thermal capacity.
°781	180	°1096	268	°1166	310	°1248	339
873	202	†1171	302	1194	318	1251	340
948	227			1197	319	1251	342
993	238			1215	327	1334	377
				1218	330	1352	367

* The corresponding chart for Table III. is almost identical with this.
† Incipient fusion (?) at the base of the crucible.

In both the tables, III. and IV., the solid points lie on lines which, if reasonably curved, would be nicely tangent to an initial specific heat of about 0·2 at °C. The grouping, in other words, is so regular as to exclude the probability of anomalous features, either in the observed or the unobserved parts of the loci. The solid point near *a* (fig. 4, a similar point occurs in Table III.) alone lies markedly above the curve ; but inasmuch as in my volume work I found solidification to set in at 1100°, it is altogether probable that the occurrence at 1170° is incipient fusion (§ 13).

The regularity of the liquid loci (Tables III. and IV.) is slightly less favourable ; but the discrepancies which occur are above 1300°, and obviously accidental (§ 10, end).

12. *Specific Heat.*—As regards the mean specific heats between 800° and 1100° in Tables III. and IV., it will be seen that the intermediate datum would satisfy both groups of points about as well as the individual data given. A tracing made of the first group practically covers the other. The same remarks may be made for the liquid state. I have not attempted any elaborate reductions, since the equations of the necessarily curved loci would have to be arbitrarily chosen, and since values for specific heat are of no immediate bearing on the present inquiry.

13. *Hysteresis.*—Recurring to the suggestion of the preceding paragraph, it appears that the fusion behaviour of rocks must be accompanied by hysteresis* of the same nature as that which I observed with naphthalene and other substances: for, whereas in my volume work with diabase I was able to cool the rock down to 1095° without solidifying it, evidences of fusion (at *a*, figs. 4 and 5) do not occur in the present work until 1170° is reached. The magnitude of the lag is thus of the order of (say) 50°, and its pressure-equivalent may be estimated as 500 atmospheres.

14. *Latent Heat.*—In virtue of the fact that the (upper) end of the solid locus (Tables III. and IV.) may be carried so near the beginning of the liquid locus, the datum for latent heat is determinable with some accuracy, in spite of its surprisingly small (relative) value. Difficulties, however, present themselves in the determination of the true melting-point, a datum which can only be sharply defined when the temperature of the crucible is quite constant throughout. I have, therefore, considered it preferable to state the conditions at 1200° and at 1100°, the former being nearer fusion and the latter very near solidification. The latent heats for these

* Am. Journal, xlii. p. 140 (1891); *cf.* ibid., xxxviii. p. 408 (1889).

temperatures are 24 and 16 respectively. The coincidence of results in both of the independent constructions (Tables III. IV.) is in a measure accidental.

15. *The Relation of Melting-point to Pressure.*—The first and second laws of thermodynamics lead to the equivalent of James Thomson's fusion equation, which in the notation of Clausius* is $dT/dp = T(\sigma - \tau)/Er'$; where T is the absolute melting-point, $\sigma - \tau$ the difference of specific volumes solid and liquid at T, r' the latent heat of fusion, and E Joule's equivalent.

Combining the present Series I. of thermal measurements with the former Series III. of volume measurements, I obtain at 1200°, since T = 1470°, $\sigma - \tau = \cdot 0394/2\cdot 72$ (where 2·72 is the density of the solid magma at zero), and $r' = 24$.

$$\left(\frac{dT}{dp}\right)_{1200} = \cdot 021\,;$$

and at 1100°, since T = 1370°, $\sigma - \tau = \cdot 0385/2\cdot 72$, and $r' = 16$,

$$\left(\frac{dT}{dp}\right)_{1100} = \cdot 029.$$

Similarly, combining the present (heat) Series II. with the former (volume) Series IV., at 1200°, since $\sigma - \tau = \cdot 0352/2\cdot 72$, and $r' = 24$,

$$\left(\frac{dT}{dp}\right)_{1200} = \cdot 019\,;$$

and at 1100°, since $\sigma - \tau = \cdot 0341/2\cdot 72$, and $r' = 16$,

$$\left(\frac{dT}{dp}\right)_{1100} = \cdot 026.$$

Hence the probable *silicate* value† of dT/dp falls within the margin (·020 to ·036) of corresponding data for organic substances (wax, spermaceti, paraffin, naphthalene, thymol). I may, therefore, justifiably infer that the relation of melting-point to pressure in case of the normal type of fusion is nearly constant irrespective of the substance operated on, and in spite of the enormous differences of thermal expansibility and (probably) of compressibility. And in the measure in which this is nearly true on passing from the carbon compounds to the thoroughly different silicon compounds, is it

* *Wärmetheorie*, i. p. 172 (1876).

† For reasons to be stated elsewhere, $\theta_m = a + \cdot 025p$ (where θ_m is the melting-point in °C. at the pressure p atmospheres) will be assumed in making geological application of the above data.

more probably true for the same substance changed only as to temperature and pressure. In other words, the relation of melting-point to pressure is presumably linear. In my work on the continuity of solid and liquid * these relations are corroborated for naphthalene within an interval of 2000 atmospheres.

XXIX. *Notices respecting New Books.*

Treatise on Thermodynamics. By PETER ALEXANDER, *M.A.* London: Longmans, Green, and Co. 1892.

FROM the preface it appears that this book is ambitious: it claims to have elevated the science of Thermodynamics into an organic unity from being a mere collection of detached propositions, to exhibit the thermodynamic relations as the outcome of physical, as opposed to mathematical, considerations, to have cleared away the fog that has enwrapped the subject of irreversibility, and, by an enlarged definition of entropy, to have opened up a mode of dealing with this subject, and, finally, to have dissipated the haziness that has overlain the subjects of Motivity and Dissipation of Energy.

The idea is to be deprecated, however, that, as hitherto treated, the science of Thermodynamics has consisted of any more detached propositions than the two, representing the two laws, which are the necessary basis of this as of every other treatise on the subject, viz. that of the conservation of energy and that of the perfection of a reversible engine or its equivalent, together with their consequences; and indeed a set of relations, which are the expressions in different forms of the same fact and which are all deducible from each other by simple transformations, does not constitute different but identical propositions. What the author has really done is to express the two laws, *i. e.* practically the values of the dynamical equivalent and of Carnot's function, in a manner even more general than that worked out (though not otherwise employed) by Clausius, viz. in terms of two general variables *with any scale of temperature whatever*, and then from these expressions to deduce particular thermodynamic relations by the substitution of particular variables: and it is these relations, which are necessarily identical, that constitute the "detached propositions" above mentioned.

Even if this method does not really tend to promote the organic unity of the science, it has without doubt its advantages and, by reason of its generality, should find place in some form or other in every formal text-book: it is certainly convenient if only as a simple mode of demonstrating certain identities and even of bringing to light identities, unimportant enough it may be, that might otherwise escape recognition. At the same time it is unlikely that general resort will be made to it for obtaining the really important

* Am. Journ. xlii. p. 144 (1891).

forms of the thermodynamic relations, each of which is patent on a glance at the corresponding infinitesimal cycle.

In his investigation of these general expressions, the author prefers not to avail himself directly of the fact that infinitesimal changes of entropy and intrinsic energy are perfect differentials, and so, according to Lord Kelvin's simple plan, to apply the corresponding criteria forthwith, this method savouring of mathematics only: he follows Clausius' original lead instead, without, however, Clausius' elaboration, and, taking an infinitesimal cycle composed of two pairs of thermal lines of any different types, he sums up the heat absorbed all round the cycle and also the changes of entropy, and equates the former sum to the area of the cycle and the latter to zero, this lengthier process being chosen as being of a more distinctly physical character than the other. In the second of these calculations the criterion of a perfect differential is of course necessarily arrived at, since the process of determining the criterion is essentially that of the method pursued; attention might therefore with advantage have been called to the mathematical character of this resulting equation, more especially as after reading Chap. XV., wherein is given Lord Kelvin's method, a student will not be likely to have recourse to the other. Advantageous, too, would be the omission in this calculation of the signs of integration, which are finally discarded as quite unnecessary and are not even introduced into the other calculation on p. 42.

With respect to irreversibility, it is pointed out that there may be processes which, though not actually reversible, are, *so far as the working substance is concerned*, in one direction equivalent to processes that are reversible, in which case the changes of entropy *that occur in the working substance itself* during such processes (termed *conditionally* irreversible, in contradistinction to *intrinsically* irreversible processes which have no such equivalents) depend only on its initial and final states. But we are not really helped by these considerations—which are not new—since it is the actual sources &c. and the actual variations of entropy with which we are really concerned.

The proposed enlargement of the definition of entropy which is to help with the treatment of irreversibility greatly needs defence. It is ushered in with an objection to the definition of the entropy of a body or system as the sum of the entropies of its parts, "which seems to me as unwarrantable as to define *the temperature of a body or system* as *the sum of the temperatures of its parts*," so that to speak of entropy per unit mass "seems to me as unwarrantable as to speak of *temperature per unit mass*"; though no reason whatever is given or even hinted for likening entropy to temperature rather than to such another physical property as energy or volume. Such a definition of entropy is then desired as will make the entropy of any system whatever invariable when no heat passes into or out of it; and the author considers that he has obtained such a definition—which satisfies also his previous objection—in the formula $\Sigma . \tau m\phi / \Sigma . \tau m$, where m is the mass

of a portion of the system of which the entropy and absolute temperature are ϕ and τ.

Assuming, however, the formula for a single mass, consider a system of two masses m_1, m_2 of the same substance with entropies ϕ_1, ϕ_2 and at absolute temperatures τ_1, τ_2 respectively; and let these masses be respectively expanded and compressed adiabatically to the temperature τ and then respectively compressed and expanded isothermally to the pressure p: the system is now in equilibrium, and, if τ is taken such that no energy is lost or gained by the system and that the heat lost by the one mass is equal to that gained by the other, it is in that state of equilibrium which the system would finally attain in isolation. If, then, ϕ is the final entropy of the system, the heats lost and gained are $m_1\tau\ (\phi_1-\phi)$ and $m_2\tau\ (\phi-\phi_2)$, whence $\phi=(m_1\phi_1+m_2\phi_2)/(m_1+m_2)$, which does not satisfy the proposed formula except for $\tau_1=\tau_2$ or $\phi_1=\phi_2$.

Entropy being thus considered a debatable subject, it is surprising to see it postulated in the Introduction as an evident property of a substance and to find it treated as such without debate or explanation till the last chapter. In Maxwell's opinion, "it is to be feared that we shall have to be taught thermodynamics for several generations before we can expect beginners to receive as axiomatic the theory of entropy."

The account given of thermodynamic motivity and dissipation of energy is good and clear, and it is properly remarked that Clausius' theorem of the tendency of the entropy of the universe to a maximum is only a restatement in terms of entropy of Lord Kelvin's dissipation theorem published thirteen years earlier.

Though the book, therefore, does not seem quite to fulfil the promise of the Preface, it will doubtless prove a useful mathematical introduction to the subject, which it does not pretend to treat experimentally, the few experiments that are referred to being mentioned only briefly and without detail.

Its arrangement seems capable of improvement. Thus, it is not broken up into articles and its equations are numbered consecutively from first to last, so that references are tedious: the theorem of the dependence on pressure of the temperature of the maximum density of water is placed where it seems to be dependent on thermodynamical considerations, while that of the equality of the ratios of the principal specific heats and of the principal elasticities is actually proved by such considerations, of which it is absolutely independent—as is obvious, since it was known to Laplace: and two general equations of very great importance, (216) and (217), are deduced only incidentally to prove that the principal specific heats of superheated vapours are approximately functions of temperature only.

There is some looseness of expression: thus the word *perfect* is used as equivalent to *efficient*, which leads to the solecisms *more perfect* and *equally perfect*; the dyne, centimetre, and erg are called *French* units: the dynamical equivalent of heat is said to be

"772 on the Fahrenheit scale"; Mayer is credited with an experiment which was repeated by Joule, whose object in experimenting is rather made to appear as the justification of Mayer's hypothesis. Technical terms, too, are used without definition: thus the idea of *efficiency* is introduced on p. 26 without any explanation though its quantitative measurement is concerned, and, indeed, when an implicit definition is finally given on p. 35 in connexion with a Carnot cycle, it is in terms which are neither general nor such as Carnot could have accepted. It may also be pointed out that in Chaps. XVI. and XVII. there is no distinguishing symbol for absolute temperature, though everywhere else the letter τ is used; that in Chapter XV. the numerical specification of entropy differs from that adopted elsewhere; and that in (151) only a particular integral is given of the partial differential equation (150), the general solution of which is $K=\tau^2 f(\tau^3-3A\tau_0{}^2p)$ corresponding to the characteristic $v/\tau=\psi(p)+A\tau_0\int d\tau\, \tau^{-2}f(\tau^3-3A\tau_0{}^2p)$.

The notation is not all that can be desired; that of partial differential coefficients is specially abused, after Clausius' example, in being applied to denote thermal capacities, and in Chap. XI. the differential coefficients of p and λ with respect to t are continually enclosed in brackets armed with some such subscript as ϕ, which is entirely incorrect, as these are not partial differential coefficients at all except with respect to the state of saturation; elsewhere, too, occurs repeatedly the meaningless form $(d\tau/dt)_\phi$, wherein τ is an acknowledged function of t only.

These are, however, blemishes which do not impair the value of the book, but might be considered in view of a second edition. Among its good points must specially be mentioned the stress that is laid on the proper definition of absolute temperature, though on p. 168 the author himself uses the definition to which he objects; and there is an interesting modification of Rankine's characteristic for gases suggested which deserves discussion. It is further well remarked that even on the caloric theory Clapeyron's version of Carnot's operations (which is that adopted in the book) would be improved by the adoption of Clausius' modification,—which, by the way, is ascribed to J. Thomson, though contained in that memoir of Clausius which first set the subject on its new basis. It may be here remarked that Carnot's own version of his cycle requires no modification whatever, even from the new point of view.

Die physikalische Behandlung und die Messung hoher Temperaturen. By Dr. Carl Barus. Leipzig: Barth, 1892.

The subject of pyrometry, although forming an important application of physics to manufactures, has not received from physicists the attention which it deserves. One reason for this is undoubtedly the difficulty of maintaining a constant high temperature, and another is to be found in the fact that the subject necessitates a detailed study of the alterations produced in the properties of matter by excessive heating. In order to measure any tempera-

ture absolutely, we must assume that some property of a substance remains constant at that temperature and at other known temperatures. If this is not the case, the same temperature will have different values according to the method by which it is measured, and its true value will most probably be that found by a majority of the methods. The author in his present volume has criticized the different methods of determining temperatures, and has given the results of experiments by himself and other workers in the same field, from which it appears that only three properties remain constant over wide ranges of temperature. These are the expansion of gases, the change of their viscosity with temperature, and the thermoelectric properties of certain metals. All these methods yield consistent results for the value of a given high temperature.

The second part of the volume is a discussion of the applicability of these three methods, and Dr. Barus pronounces in favour of the thermoelectric method. He then goes on to discuss the various forms of apparatus which might be used in applying this method; from which it appears that a junction of platinum with an alloy of platinum and iridium or rhodium gives the best results.

The book is the outcome of several years of difficult experimenting, and it is to be hoped that it will encourage a closer study of the properties of bodies, and especially of metals, at high temperatures. JAMES L. HOWARD.

Hülfsbuch für die Ausführung elektrischer Messungen. *By* Dr. AD. HEYDWEILLER. Leipzig: Barth, 1892.

THIS volume is not intended to serve as a text-book, but merely as an epitome of the various processes of electrical measurement. It gives in a collected form the different methods available for any particular kind of measurement, together with a short description of each; the formulæ necessary in order to calculate the results being likewise quoted, but not proved. In the majority of cases, however, the original papers and treatises are referred to for more complete information on this latter point. Under each experiment the author mentions the sources of error to which it is liable, and the devices for avoiding or eliminating them are stated, when such exist. This portion of the work has been carefully written, and will be found useful when the choice of a suitable method of measurement has to be made. At the end of the volume the various electrical constants have been tabulated, and four-figure logarithm and trigonometrical tables are also to be found there. Although the title of the book refers to electricity only descriptions of magnetic observations have also been given; but, as the author tells us in his preface, these are treated more briefly, and only those which are necessary in electrical measurements have been described. JAMES L. HOWARD.

XXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 150.]

December 21st, 1892.—Prof. J. W. Judd, F.R.S., Vice-President, in the Chair.

THE following communications were read :—

1. "On a Sauropodous Dinosaurian Vertebra from the Wealden of Hastings." By R. Lydekker, Esq., B.A., F.G.S.

2. "On some additional Remains of Cestraciont and other Fishes in the Green Gritty Marls, immediately overlying the Red Marls of the Upper Keuper in Warwickshire." By the Rev. P. B. Brodie, M.A., F.G.S.

3. "*Calamostachys Binneyana*, Schimp." By Thomas Hick, Esq., B.A., B.Sc.

4. "Notes on some Pennsylvanian Calamites." By W. S. Gresley, Esq., F.G.S.

5. "Scandinavian Boulders at Cromer." By Herr Victor Madsen, of the Danish Geological Survey.

During a visit to Cromer in 1891 the author devoted much attention to a search for Scandinavian boulders, and obtained three specimens; one (a violet felspar-porphyry) was from the shore, and the other two were from the collection of Mr. Savin. The first was considered to come from S.E. Norway, and indeed Mr. K. O. Björlykke, to whom it was submitted, refers it to the environs of Christiania.

The author considered that the two specimens presented to him by Mr. Savin, who had taken them out of Boulder Clay between Cromer and Overstrand, were from Dalecarlia; and these were submitted to Mr. E. Svedmark, who compared one of them (a brown felspar-hornblende-porphyry) with the Grönklitt porphyry in the parish of Orsa, and declared that the other (a blackish felsite-porphyry) might also be from Dalecarlia.

January 11th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read :—

1. "Variolite of the Lleyn, and associated Volcanic Rocks." By Catherine A. Raisin, B.Sc.

The district in which these rocks occur is the south-western part of the Lleyn peninsula, marked on the Geological Survey map as 'metamorphosed Cambrian.'

Some of the holocrystalline rocks are probably later intrusions. The igneous rocks, which are described in detail in the present paper, belong to the class of rather basic andesites or not very basic basalts; they show two extreme types, which were probably formed by

differentiation from an originally homogeneous magma. Corresponding to the two types of rock are two forms of variolite. These are fully described, and their mode of development is discussed.

The variolites occur near Aberdaron and at places along the coast. Their spherulitic structure often is developed towards the exterior of contraction-spheroids, and in this and in other particulars they correspond with those of the Fichtelgebirge and of the Durance. The volcanic rocks include lava-flows and fragmental masses, both fine ash and coarse agglomerate. They are associated with limestones, quartzose, and other rocks, which are possibly sedimentary, but which give no trustworthy evidence of the age of the variolites.

2. "On the Petrography of the Island of Capraja." By Hamilton Emmons, Esq.

The rocks of Capraja consist generally of andesitic outflows resting on andesitic breccias and conglomerates. The southern end seems to have formed a distinct centre of volcanic activity, whose products are younger in age and more basic in character than the rocks of the rest of the island, and may be termed 'anamesites.' The lavas appear to have flowed from a vent at some distance from the cone which probably occurred here and gave out highly scoriaceous fragments. In the other parts of the island andesite is almost everywhere found, with patches of the underlying breccias here and there in the valley bottoms. The chief centre of activity probably lay west of the centre of the island.

Petrographical details of the andesites and anamesites, descriptions of the groundmass and included minerals of each, and chemical analyses are given. As regards the age of the constituents, the author arranges them in the following order, commencing with the oldest:—magnetite, olivine, augite, mica, felspar, nepheline.

XXXI. *Intelligence and Miscellaneous Articles.*

ON A NEW ELECTRICAL FURNACE. BY M. HENRI MOISSAN.

THIS new furnace is made of two carefully plane pieces of quicklime one placed under the other. In the lower one is a longitudinal groove for the two electrodes, and in the middle is a small cavity more or less deep acting as a crucible; it contains a layer of a few centimetres of the substance to be acted upon by the arc. A small carbon crucible may also be placed in it containing the substance to be calcined. In the reduction of oxides and the fusion of metals, larger crucibles are used, and through a cylindrical aperture in the upper brick small cartridges of the compressed oxide and carbon can from time to time be added. The diameter of the carbons which act as conductors will of course vary with the strength of the current; after each experiment the end of the carbon is changed into graphite.

The current most frequently used was one of 30 amperes and

55 volts; the temperature did not much exceed 2250°. A current furnished by a gas-engine of 8 horse-power was 100 amperes and 45 volts produced a temperature of about 2500°. Finally, thanks to the courtesy of M. Violle, we had at our disposal 50 horse-power; the arc in these conditions measured 450 amperes and 70 volts, the temperature was about 3000°.

With high-tension experiments certain precautions must be taken and the conductors be carefully insulated. Even with currents of 30 amperes and 50 volts, like those used at the beginning of the investigation, the face must not be exposed to a prolonged action of the electrical light, and the eyes must always be protected by means of very dark glasses. Electrical sun-strokes were very frequent at the outset of these researches, and the irritation produced by the arc on the eyes may produce very painful congestion.

The temperatures given are only approximate; they will be especially determined by M. Violle by methods to be afterwards described. A certain number of the results obtained are briefly enumerated.

When the temperature is near 2500°, lime, strontia, and magnesia crystallize in a few minutes. If the temperature reaches 3000° the substance of the furnace itself—quick-lime—melts and runs like water. At this same temperature carbon rapidly reduces calcic oxide, and the metal is liberated freely; it unites readily with the carbon of the electrodes, forming a calcic carbide, liquid at a red heat, and which can be easily collected. Chromic oxide and magnetic oxide of iron are melted rapidly at a temperature of 2250°. Uranium oxide when heated alone is reduced to protoxide, crystallizing in long prisms. Uranium oxide, which cannot be reduced by carbon at the highest temperature of our furnaces, is reduced at once at the temperature of 3000°. In ten minutes it is easy to obtain a regulus of 120 grains of uranium.

The oxides of nickel, cobalt, manganese, and chromium are reduced by carbon in a few minutes at 2500°. This is a regular lecture experiment not requiring more than a quarter of an hour.

By this method we have been able to cause boron and silicon to act on metals, and thus obtain borides and silicides in very beautiful crystals.

This investigation is being continued.—*Comptus Rendus*, Dec. 12, 1892.

ON THE DAILY VARIATIONS OF GRAVITY. BY M. MASCART.

I have on former occasions used under the name of a *gravity barometer* an instrument by which the variation of gravity between different stations may be determined. The apparatus has the drawback of being very fragile, but the same arrangement has great advantages in examining whether there are temporary variations in one and the same place.

For some years past I have arranged a barometric tube containing a column of mercury four metres and a half in length, which

counterbalances the pressure of a mass of hydrogen contained in a lateral vessel. The whole apparatus is sunk in the ground with the exception of a short column of mercury at the top. The level of the liquid is compared with a lateral division, the image of which is formed in the axis of the tube, and the points may be fixed to within the $\frac{1}{100}$ of a millimetre.

Direct observations at different times of day only showed a continuous course, the greater part of which was due to inevitable changes of temperature; certain results can only be obtained by photographic registration.

In the proofs submitted the differences of level are multiplied by 20; they correspond to the variations which are directly observed on a column 90 metres in length.

The curves ordinarily present a very regular and slow course which is especially due to changes of temperature; but for some days sudden accidents are seen, the duration of which is from fifteen minutes to an hour, and which do not seem to be explicable otherwise than by correlated variations of gravity. These accidents may attain and even exceed $\frac{1}{20}$ of a millimetre, which corresponds to $\frac{1}{90000}$ or one second per day, supposing that they lasted the whole day.

In order to have a term of comparison, it is sufficient to observe that if the difference between high and low water is 10 metres, the liquid layer would produce a variation of $\frac{1}{500000}$ of the level value of gravity, that is one fifth of the preceding.

The existence of these temporary variations of gravity appears undoubted and deserves attention. I intend to organize at the Observatory of the Parc Saint Maur an apparatus constructed with more care, from which all casual trepidation of the ground is excluded, and the indications of which can be continuously followed.

Observations of this kind will no doubt present a peculiar interest in volcanic districts if the changes are due to displacements of masses in the interior.—*Comptes Rendus*, January 30, 1893.

PRELIMINARY NOTE ON THE COLOURS OF CLOUDY CONDENSATION. BY C. BARUS.

By allowing saturated steam to pass suddenly from a higher to a lower temperature (jet) in uniformly temperatured, uniformly dusty air, the following succession of colours is seen by transmitted white light, if the difference of temperature in question continually increases:—Faint green, faint blue, pale violet, pale violet-purple, pale purple, muddy brown-orange, straw-yellow, greenish yellow; green, blue-green, grey-blue, intense blue, indigo, intense dark violet, black (opaque); intense brown, intense orange, yellow, white.

Seen by reflected white light, the same mass of steam is always dull neutral white.

If the colours enumerated be taken in the inverse order, beginning with white, they are absolutely identical with the interference-colours of thin plates (Newton's rings) of the first and

second order, seen by transmitted white light under normal incidence. Thus it is worth inquiring whether small globules of water, when white light is normally transmitted, affect it like thin plates. For a given homogeneous colour, if I be the intensity of the incident light and k (04 to ·05) the reflexion-coefficient, then after a single transmission the interference maxima and minima are

$$(1-k)^2(1+k^2)\mathrm{I} \quad \text{and} \quad (1-k)^2(1-k^2)\mathrm{I};$$

they differ only very slightly. But if there be an indefinite number of particles all of the same size available, then this process is indefinitely repeated in such a way that while the coloured light is not extinguished, the admixed white light becomes continually more coloured. Hence, after a sufficiently great number of transmissions, the emergent ray will show intense colour. Seen by reflected light, the case is almost the converse of this. For a single particle the masses which interfere are (kI and $k(1-k)^2$I) weaker, but nearly equal, and the interference is therefore very perfect. It is not, however, capable of indefinite repetition, for after each interference the direction is reversed. The light which emerges in a direction opposite to the incident ray must therefore have passed through the particles, *i. e.* it has been brought to interference both by reflexion and by transmission, and its colour is thus virtually extinguished.

The final point to be considered is the occurrence of black between brown and dark violet of the first order. Here, however, for relatively very small increase of the thickness of the plate, the colours run rapidly from brown through red, carmine, dark red-brown to violet. Hence these interferences are apt to occur together and an opaque effect is to be anticipated. Particularly is this presumable, because the opaque field is coincident with the breakdown of the steady motion * of the jet.

Thus it seems that the colours of cloudy condensation may, without serious error, be interpreted as a case of Newton's interferences by transmitted light. In so far as this is true, one may pass at once from the colour of the field to the size of the particles producing it; and the dimensions so obtained agree well with R. v. Helmholtz's estimate made in accordance with Kelvin's equation for the increase of vapour-tension at a convex surface. In the study of the condensation phenomena vapour-liquid, the experimental power of a method, which is adapted for *instantaneous* observation, and which, for a certain range of dimensions, not only discriminates between vapour and a collection of indefinitely small suspended water-globules, but actually defines their size, cannot be overestimated. An account of my work, together with other allied observations, will be given in the March number of the 'American Meteorological Journal.'—*Silliman's Journal*, February 1893.

* I refer here to Osborne Reynolds' work (Phil. Trans. iii. p. 935, 1883) with liquid jets, according to which, after a certain critical velocity is surpassed, the uniformly steady motion breaks up into eddying motion. I am also searching for Reynolds' lag phenomenon (*l. c.* p. 957).

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[FIFTH SERIES.]

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XXXII. *On Plane and Spherical Sound-Waves of Finite Amplitude.* *By* CHARLES V. BURTON, *D.Sc.**

PART I.—PLANE WAVES.

1. THE subject of plane waves of finite amplitude has been considered by Riemann†; and so long as we confine our attention to the case where velocity and density are everywhere continuous, his investigation, as is well known, leaves little to be desired. It will not, therefore, be necessary here to make further reference to this aspect of the subject; but there is one part of Riemann's work which Lord Rayleigh has clearly shown to be unsatisfactory, and it is this point which we have now especially to consider. Lord Rayleigh says‡:—

"..... It has been held that a state of motion is possible in which the fluid is divided into two parts by a surface of discontinuity propagating itself with constant velocity, all the fluid on one side of the surface of discontinuity being in one uniform condition as to density and velocity, and on the other side in a second uniform condition in the same respects. Now, if this motion were possible, a motion of the same kind in which the surface of discontinuity is at rest would also be possible, as we may see by supposing a velocity equal and

* Communicated by the Physical Society: read February 24, 1893.

† "Ueber die Fortpflanzung ebener Luftwellen von endlicher Schwingungsweite," *Gött. Abhandl.* t. viii. (1860); reprinted in *Werke*, p. 145.

‡ Theory of Sound, vol. ii. § 253, p. 41.

opposite to that with which the surface of discontinuity at first moves, to be impressed upon the whole mass of fluid. In order to find the relations which must subsist between the velocity and density on the one side (u_1, ρ_1) and the velocity and density on the other side (u_2, ρ_2), we notice in the first place that by the principle of the conservation of matter $\rho_2 u_2 = \rho_1 u_1$. Again, if we consider the momentum of a slice bounded by parallel planes and including the surface of discontinuity, we see that the momentum leaving the slice in the unit of time is for each unit of area $(\rho_2 u_2 = \rho_1 u_1) u_2$, while the momentum entering it is $\rho_1 u_1^2$. The difference of momentum must be balanced by the pressures acting at the boundaries of the slice, so that

$$\rho_1 u_1 (u_2 - u_1) = p_1 - p_2 = a^2(\rho_1 - \rho_2),$$

whence

$$u_1 = a\sqrt{\left(\frac{\rho_2}{\rho_1}\right)}, \quad u_2 = a\sqrt{\left(\frac{\rho_1}{\rho_2}\right)}.$$

The motion thus determined is, however, not possible; it satisfies indeed the conditions of mass and momentum, but it violates the condition of energy expressed by the equation

$$\tfrac{1}{2} u_2^2 - \tfrac{1}{2} u_1^2 = a^2 \log \rho_1 - a^2 \log \rho_2."$$

2. The assumed motion here criticised is one in which density and velocity are constant for all points on the same side of the surface of discontinuity, while this surface itself is propagated through the fluid with constant velocity. It is easily shown, however, that the same objection applies when, on either side of the surface, velocity and density vary continuously in the direction of propagation, while the velocity of propagation of the surface is also allowed to vary. For let S (fig. 1) be a surface of discontinuity which is being propagated through the fluid, while the planes A, B, parallel to S and lying on either side of it, are fixed in the fluid. At a given instant let

Fig. 1.

distance of S from A $= m$,

" B " S $= n$;

density and velocity of fluid just to the left of S $= \rho_1$, u_1,

density and velocity of fluid just to the right of S $= \rho_2$, u_2;

velocity with which S is travelling $=$ V.

Then, since A and B are fixed in the fluid, they are approximately moving with the respective velocities u_1, u_2; m and n being taken sufficiently small. On the same understanding, the mass of fluid between A and B (referred to unit surface) $=m\rho_1+n\rho_2$; and since this mass must remain constant,

$$\frac{d}{dt}(m\rho_1+n\rho_2)=0;$$

i. e. in the limit, when m and n are infinitesimal,

$$\rho_1\frac{dm}{dt}+\rho_2\frac{dn}{dt}=0,$$

or

$$\rho_1(\mathrm{V}-u_1)=\rho_2(\mathrm{V}-u_2). \quad . \quad . \quad . \quad . \quad . \quad (1,$$

Similarly, if p_1 and p_2 are the pressures corresponding to ρ_1 and ρ_2, the principle of momentum gives:—

$$\begin{aligned} p_1-p_2 &= \text{rate of change of momentum between A and B} \\ &= \frac{d}{dt}(u_1\rho_1 m+u_2\rho_2 n) \\ &= u_1\rho_1(\mathrm{V}-u_1)-u_2\rho_2(\mathrm{V}-u_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

If the energy per unit volume corresponding to density ρ (in the absence of bodily motion) is called $\chi(\rho)$, the principle of energy would further give

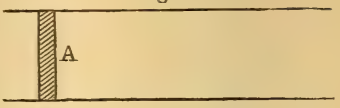
$$\begin{aligned} p_1u_1-p_2u_2 &= \text{rate of change of energy between A and B} \\ &= \frac{d}{dt}\left\{m\left(\tfrac{1}{2}\rho_1u_1^2+\chi(\rho_1)\right)+n\left(\tfrac{1}{2}\rho_2u_2^2+\chi(\rho_2)\right)\right\} \\ &= \left\{\tfrac{1}{2}\rho_1u_1^2+\chi(\rho_1)\right\}(\mathrm{V}-u_1)-\left\{\tfrac{1}{2}\rho_2u_2^2+\chi(\rho_2)\right\}(\mathrm{V}-u_2). \quad (3) \end{aligned}$$

Since (1), (2), and (3) involve only the instantaneous values of u_1, ρ_1, u_2, ρ_2, and V, together with explicit functions of such values, while the space- and time-variations of all these quantities are absent from the equations, it is evident that the conditions to be satisfied at the surface S are the same as if u_1, ρ_1, u_2, ρ_2, V were absolute constants. We conclude then, that, *with our assumptions*, a surface of discontinuity cannot be propagated through a fluid with any velocity, uniform of variable, except under that special law of pressure for which progressive waves are of accurately permanent type.

3. What, then, becomes of waves of finite amplitude after discontinuity has set in? We may emphasize this difficulty, and at the same time obtain a clue to its solution, by considering the following case (fig. 2):—A is a piston fitting a

cylindrical tube (or, if we please, is a portion of an unlimited rigid plane). All the air to the right of A is initially at rest and of uniform density, and then A is impulsively set in motion, and kept moving to the right with uniform velocity v. Consider the speed with which the disturbance generated by A advances into the still air to the right; it is evident that in all cases the front of the disturbance must advance faster than A. Take, then, the case in which

Fig. 2.



$$v > a,$$

where a is the propagation-velocity of infinitesimal disturbances. Two alternatives present themselves:—

(i.) If velocity and density are always either constant or *continuously* variable in the direction of propagation, the rate of propagation at any point will, in accordance with known principles, be

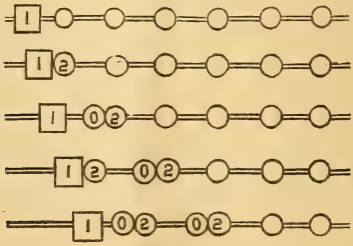
$$\sqrt{\frac{dp}{d\rho}} + u,$$

and therefore at the front of the disturbance, where $u=0$ and $\rho =$ the "undisturbed" density, the velocity of propagation will be simply $=a$; that is, *less* than the velocity with which A is advancing. Obviously this will not do.

(ii.) If velocity and density are *not* always either constant or continuously variable, that is, if one or more surfaces of discontinuity are being propagated through the air, we are met by the difficulty explained in the last section.

4. A simple mechanical analogy will help to indicate the actual motion. A number of equal spheres, of the same material throughout, are capable of sliding without friction

Fig. 3.



along a straight bar (fig. 3), and are connected together by a number of very weak and exactly similar springs (not shown), so that when there is equilibrium they are equally spaced

along the bar. If one of the spheres were moved backwards and forwards through a small range, a disturbance would travel through the whole system, but owing to the weakness of the connecting springs it would travel very slowly. Suppose, now, that the last sphere on the left hand is connected to a movable piston by a spring half the length of the others, but otherwise similar to them; and let this piston be suddenly moved to the right with a considerable velocity which is kept constant, and which we may call unity. The weak connecting spring between the piston and the first sphere produces no sensible effect until the two are almost in contact, when the sphere rebounds with velocity 2. This first sphere then strikes the second, imparting to it the velocity 2, and at the same time coming to rest. The positions of the spheres after successive equal intervals of time are represented in fig. 3, where the number written on any sphere represents its velocity just *after* the impact which it is suffering. No number is written on those spheres which have not so far been affected by the motion. From this it will be evident that when the piston moves to the right with a constant velocity which is very great compared with the propagation-velocity of infinitesimal vibrations of the system, the disturbance advances to the right with twice the velocity of the piston, provided that the diameters of the spheres are excluded from the reckoning.

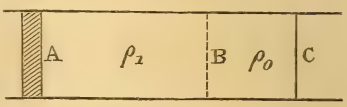
Now suppose that the spheres are too small and too close together to be individually distinguished; then, at any instant, the system will appear to be divisible into two parts, in one of which the velocity is unity, while in the other it is zero; and in the moving part the spheres will appear to be twice as thickly condensed as in the still part. That the constant velocity of the piston is very great compared with the propagation-velocity of small vibrations is of course only a supposition introduced for the sake of simplicity. If, on the other hand, these two velocities are comparable, two adjacent spheres will always remain finitely separated from one another, and the velocity of any individual sphere within the disturbed stretch will never be as small as zero, or as great as twice the velocity of the piston; the *mean* velocity within the disturbed stretch being equal to that of the piston. When the spheres are very small and very close together, we shall still have apparently an abrupt transition from finite velocity and greater density to zero velocity and smaller density; and the energy, which is apparently lost as the spheres pass from the latter condition to the former, exists as energy of relative motion and unequal relative displacement amongst the spheres in the disturbed stretch.

5. Let us now compare the case just considered with the

case of § 3 (fig. 2): and first, concerning the nature of the analogy, it should be noticed that the individual spheres are not the analogues of the separate gaseous molecules, but that when both spheres and molecules are very small and very numerous, the apparently continuous properties of the system of spheres correspond to similar properties of the gas. The connecting springs represent the elasticity of the gas, isothermal or adiabatic as the case may be, and the energy of relative motion and unequal relative displacement amongst the disturbed spheres *suggests* that there is a production of heat over and above that which would be due to the (isothermal or adiabatic) change of density; that is, *a dissipative production of heat*. The motion considered in the last section properly corresponds to the case where there is no conduction of heat, so that the connecting springs are the representatives of *adiabatic* elasticity, and the additional heat generated remains wholly within the more condensed part of the air. If we make the somewhat violent assumption that the temperature of the air remains constant throughout, the additional heat generated will be conducted away isothermally, and the equivalent energy will be, for our purposes, entirely lost. To represent this case by means of our spheres we should have to regard the connecting springs as representing isothermal elasticity, while the energy of relative motion and unequal relative displacement among the disturbed spheres, as fast as it is produced, is to be consumed in doing work against suitable internal forces.

6. The mechanical system of spheres and springs, having suggested a solution, has served its purpose, and it now remains for us more closely to consider the aerial problem in the light of this suggestion. We may take, first, the case where the temperature is supposed to be invariable; for although such a supposition is necessarily far removed from the truth, it leads to very simple results, which indicate well enough the general character of the motion. Let the piston A (fig. 4) be moving to the right with constant velocity v (which may be either less or greater than a, the velocity of feeble sounds in air). Assume all the air between A and a parallel plane surface B to have the velocity v and density ρ_1, while all the air to the right of B is at rest and has the density ρ_0. Let the plane B move to the right with velocity V. Then the invariability of mass between A

Fig. 4.



and a plane C fixed in the still air gives

$$\rho_1(V-v)-\rho_0 v=0\,; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

while from the principle of momentum,

$$\rho_1 v(V-v)=p_1-p_0\,; \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the pressure p being a function of ρ only, since the temperature is supposed to be constant throughout. If we assume for this case the truth of Boyle's law, so that $p=a^2\rho$ always, (5) becomes

$$\rho_1(a^2-Vv+v^2)=\rho_0 a^2, \quad . \quad . \quad . \quad . \quad (6)$$

which together with (4) is sufficient to determine V and ρ_1 when v and ρ_0 are given. Taking all these quantities to remain constant throughout the motion, we see that at each instant the following conditions are satisfied:—

(i) Every necessary condition between A and B, since density and velocity are there constant with respect to space and time;

(ii) Every necessary condition to the right of B, since the air there is at rest and in a constant uniform state;

(iii) Equality between the velocity of A and that of the air in contact with it;

(iv) At B, the conservation of mass and momentum, which are *necessary* conditions, and which, together with our supposition that the temperature is somehow maintained uniform, are *sufficient* to determine what takes place at B *.

Moreover, if at a time t (reckoned from the instant when A was impulsively started into motion) we take the distance of B from A to be $(V-v)t$, so that initially B coincides with A, the initial conditions are satisfied.

Thus the assumed motion satisfies all the necessary conditions; it is therefore the actual motion.

7. Let us now examine what occurs when no heat is allowed to pass by conduction or radiation; a state of things much more nearly realized in practice. Suppose the motion of A and the condition of the undisturbed air to be the same as in the last section, while the (constant) velocity of B is now called V', and the density and pressure of the air between A and B (called ρ', p' respectively) are also taken to be uniform and constant. At each instant, in place of (4) and (5), we shall now have

$$\rho'(V'-v)-\rho_0 v=0, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\rho' v(V'-v)=p'-p_0. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* Energy appears to be lost, because dissipatively produced heat is conducted away isothermally.

Since we assume that there is no transference of heat by conduction or radiation, the rate at which the *total* energy of the system increases must be equal to the rate at which work is being done upon it by the piston A. Let θ_0 be the absolute temperature to the right of B, that between A and B being θ', and let us further assume for simplicity that

$$\frac{p}{\rho\theta} = \text{a const.};$$

while γ, the ratio of the two specific heats, is also supposed constant. It can then be shown without difficulty that the total energy *per unit mass* between A and B exceeds that to the right of B by

$$\frac{p_0}{(\gamma-1)\rho_0}\frac{\theta'-\theta_0}{\theta_0}+\frac{v^2}{2};$$

and multiplying this by $\rho_0 V'$, the mass of air which crosses one unit of the surface B in each unit of time, we obtain the rate (referred to unit area) at which the system is gaining energy. Again, the rate at which unit area of the piston does work on the system

$$=p'v=p_0\frac{\rho'\theta'}{\rho_0\theta_0}\cdot v,$$

and equating this to the rate of gain of energy, we obtain

$$p_0\frac{\rho'\theta'}{\rho_0\theta_0}v=\rho_0 V'\frac{v^2}{2}+\frac{p_0 V'}{(\gamma-1)\theta_0}(\theta'-\theta_0). \quad . \quad . \quad (9)$$

We may also write equation (8) in the form

$$\rho' v(V'-v)=\frac{p_0}{\rho_0\theta_0}(\rho'\theta'-\rho_0\theta_0); \quad . \quad . \quad . \quad (10)$$

and (7), (9), and (10) will then serve to determine V', ρ', θ' when v, ρ_0, θ_0 are given. Since we have taken all these quantities to remain constant throughout the motion, we see, as before, that at each instant all the necessary conditions are satisfied; the principles of mass and momentum, together with our supposition that there is no exchange of heat, being sufficient to determine what takes place at B. Again, if at a time t from the commencement of the motion we take the distance of B from A to be $(V'-v)t$, so that initially B coincides with A, the initial conditions are satisfied. The assumed motion thus satisfies all the necessary conditions, and is therefore the actual motion.

8. If we compare the results of the last two sections with

those given by Riemann*, we shall find complete accordance so far as § 6 is concerned, though with § 7 the case is different; and this may be easily explained. We cannot in general investigate the motion of a (frictionless) compressible fluid by means of the equations of continuity and momentum, without further making some supposition as to the exchange or non-exchange of heat, and so we usually assume either that the temperature remains constant, or that there is no exchange of heat: in either case (provided the motion is continuous), the pressure is a function of the density only. At a surface of discontinuity there is not only the ordinary heating effect due to compression, but also, as we have seen, a dissipative generation of heat, and so, when applying the equations of continuity and momentum at such a surface, we must know what becomes of this additional heat. Now in all cases Riemann makes the assumption that the pressure is a function of the density only, and this is necessarily equivalent to an assumption concerning the transference of heat. Throughout most of his treatment of waves of discontinuity Riemann assumes that temperature is constant and that Boyle's law holds good; accordingly our § 6 is entirely in harmony with his conclusions, in fact (4) and (5) are only particular forms of equations given by Riemann. Of course the hypothesis that a portion of gas can be instantaneously compressed to a finite extent without any appreciable change of temperature, is not in accordance with experience, *but provided we accept the assumption that the temperature remains constant throughout, all that Riemann says concerning the propagation of waves of discontinuity under Boyle's law will hold good.*

The assumption made in § 7, that there is no appreciable transference of heat, is probably much nearer the truth; but this is not in accordance with any assumption made by Riemann. When pressure is assumed to be a function of density only, and to vary with it according to the adiabatic law, *it is virtually assumed that at the discontinuity just so much heat remains in the gas as would be due to slow adiabatic compression, while the further amount of heat which is dissipatively produced is completely and instantaneously removed by conduction.* But though Riemann's results may thus be justified by impossible assumptions concerning the diffusion of heat, we may more reasonably, following Lord Rayleigh, regard them as involving a destruction of energy. The real source of error lies in Riemann's fundamental hypothesis. At the outset he supposes the expansion and contraction of

* *Loc. cit.*

the air to be either purely isothermal or purely adiabatic, and thenceforward he treats the air as a frictionless and mathematically continuous fluid, in which pressure and density are connected by an invariable law. But in general the existence of such a fluid is contrary to the conservation of energy; for as soon as discontinuity arises, energy will be destroyed.

9. It may not be out of place to conclude this portion of the subject by a short reference to a paper by Dr. O. Tumlirz *. This author starts, as Riemann did, with the assumption that the pressure is a function of the density only, the law of pressure being further assumed to be the adiabatic law; and in order to avoid Riemann's error, he explicitly uses the principle of energy applicable to continuous motion, in place of the principle of momentum. But the foregoing discussion will have made it clear, I think, that the solution of the difficulty is not to be sought for in this direction. In addition to the assumptions common to his own work and to that of Tumlirz, Riemann uses only the principle of mass and the principle of momentum; and since by their aid alone he arrives at a completely determinate motion, it follows that any other motion consistent with the same arbitrary assumptions, and with the condition of mass, must violate the condition of momentum. We have seen, in fact, that there is dissipation of energy at a surface of discontinuity, so that the condition of energy applicable to continuous motion ceases to hold good. We are acquainted, too, with other instances where loss of continuity involves dissipation of energy; for example, there is the case of one hard body rolling over another.

As the result of his investigation, Dr. Tumlirz concludes that as soon as a discontinuity is formed it immediately disappears again, this effect being accompanied by a lengthening of the wave and a more rapid advance of the disturbance. In this way, therefore, he seeks to explain the increased velocity of very intense sounds, such as the sounds of electric sparks investigated by Mach †. But it has already been pointed out [§ 3 (i.)], that *when density and velocity are everywhere continuous functions of the coordinates*, the *front* of a disturbance advancing into still air must travel forward with the velocity of infinitely feeble sounds. A greater velocity can only ensue when the motion has become discontinuous.

* "Ueber die Fortpflanzung ebener Luftwellen endlicher Schwingungsweite," *Sitzungsb. der Wien. Akad.* xcv. pp. 367–387 (1887).

† *Sitzungsb. der Wien. Akad.* lxxv., lxxvii., lxxviii. *Cf.* also W. W. Jacques [On Sounds of Cannon], Amer. Journ. Sci. 3rd ser. xvii. p. 116 (1879).

Part II.—Spherical Waves.

10. When plane waves of finite amplitude are propagated through a frictionless compressible fluid, discontinuity must always occur sooner or later, and a moment's consideration will show that there are at least some cases when the motion in spherical waves becomes discontinuous; the question arises whether in any case it is possible (in the absence of viscosity) for divergent spherical waves to travel outward indefinitely without arriving at a discontinuous state. This question was suggested to me by Mr. Bryan, who at the same time kindly handed me notes of his manner of attacking the problem. His method was to write down the exact kinematical equation for spherical sound-waves, and then to obtain successive approximations to the integral of this equation. If it appears that after any number of approximations the integral would remain convergent for large values of the radius, we may conclude that our equation holds good throughout, and hence that no discontinuity arises. If, on the other hand, the second or any higher approximation becomes divergent for large values of the radius, it is probable that the motion becomes somewhere discontinuous. This method I have not followed out; but by another method which is, I hope, sufficiently conclusive, I shall now endeavour to show that discontinuity must always arise.

The case in which the motion loses its continuity comparatively early requires no further consideration here; we have only to concern ourselves with the case in which the initial disturbance has spread out into a spherical shell of very small disturbance whose mean radius is very great compared with the difference between its extreme radii. The equations applicable to the disturbance are then, very approximately,

$$u = a\frac{\delta\rho}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$u \text{ or } a\frac{\delta\rho}{\rho} \propto \frac{1}{r} \text{ for a given part of the wave,} \quad . \quad (12)$$

where ρ is the mean density, $\rho + \delta\rho$ the actual density at a point where the velocity is u, and a is the velocity of infinitely feeble sounds in air of density ρ; r is as usual the distance of a point from the centre of symmetry. Let us consider two neighbouring points M and N, on the same radius, *each being fixed in a definite part of the wave*, the point M being *behind* N (*i. e.* nearer to the origin), and the air-velocity at M exceeding that at N by Δu. Then, as the wave advances, each

part of it will be instantaneously moving forward with (very approximately) the velocity

$$\sqrt{\frac{dp}{d\rho}}+u,$$

determined by the corresponding values of ρ and u; so that M will be gaining on N at the rate

$$\Delta u+\frac{d}{d\rho}\sqrt{\frac{dp}{d\rho}}\cdot\frac{d\rho}{du}\Delta u \quad . \quad . \quad . \quad . \quad . \quad (13)$$

approximately. We may admit then that the rate at which M gains on N is

$$\text{never} < \mathrm{B}\Delta u,$$

where B is a constant suitably chosen.

Again, if $\Delta_0 u$ is the difference between the air-velocities at M and N at the time $t=0$, and r_0 is the corresponding co-ordinate of M, we may admit that

$$\Delta u \text{ is never } < \frac{\mathrm{A}r_0}{r_0+at}\Delta_0 u,$$

where A is a constant not very different from unity. Thus M gains on N at a rate which is

$$\text{never} < \mathrm{AB}\frac{r_0}{r_0+at}\Delta_0 u;$$

and between the times $t=0$ and $t=t_1$ the distance gained by M relatively to N will be

$$\text{at least } \mathrm{AB}\Delta_0 u\int_0^{t_1}\frac{r_0 dt}{r_0+at},$$

$$i.\,e. \qquad \text{at least } \mathrm{AB}\Delta_0 u\frac{r_0}{a}\log\frac{r_0+at_1}{r_0}. \quad . \quad . \quad . \quad (14)$$

If B is finite and positive this expression increases indefinitely with the time, so long as the laws of continuous motion hold good. If $\Delta_0 r$ was the distance between M and N at time $t=0$, the time required for M to *overtake** N will be *not greater* than the value of t_1 given by

$$-\Delta_0 r=\mathrm{AB}\Delta_0 u\frac{r_0}{a}\log\frac{r_0+at_1}{r_0};$$

or, when M and N are taken indefinitely close together at starting, by

$$\log\frac{r_0+at_1}{r_0}=\frac{a}{r_0}\div\left\{\mathrm{AB}\left(-\frac{\partial u}{\partial r}\right)_0\right\};$$

$$i.\,e., \text{ we have } t_1 \overset{=}{<} \frac{r_0}{a}\left(e^{\frac{a}{r_0}\div\left\{\mathrm{AB}\left(-\frac{\partial u}{\partial r}\right)_0\right\}}-1\right), \quad . \quad . \quad (15)$$

* *Cf.* Lord Rayleigh, 'Theory of Sound,' vol. ii. p. 36.

which gives us a finite upper limit to the time required for discontinuity to set in, provided B is finite. As our assumptions only remain approximately true so long as the motion is continuous, (15) will only give an approximation to the time when discontinuity first commences, and accordingly the relation must be taken to refer to that part of the wave for which its right-hand side is a minimum. If B is negative (which is not the case for any known substance), the appropriate part of the disturbance will be such that $\partial u/\partial r$ is positive.

To determine approximately the value of B, we may refer to (13) and the inequality immediately following. If we assume Boyle's law of pressure, so that $\sqrt{(dp/d\rho)}=\text{const.}$, we have evidently

$$B=1 \text{ very nearly.}$$

If we assume that the changes of density take place adiabatically, so that $p \propto \rho^\gamma$ and γ is nearly constant, the approximate value of B becomes

$$1+\frac{d}{d\rho}\sqrt{\frac{dp}{d\rho}}\cdot\rho\div\sqrt{\frac{dp}{d\rho}}$$

by means of (11);

$$=\frac{\gamma+1}{2}.$$

If, then, viscosity be neglected, we must conclude that under any practically possible law of pressure the motion in spherical sound-waves always becomes discontinuous, and *à fortiori* the same will be true of cylindrical waves. But inasmuch as our result for spherical waves depends on the existence of an infinite *logarithm* in (14) when t_1 is increased without limit, we may conclude that for waves diverging in four dimensions (or, more generally, in any number of dimensions finitely greater than three) there would be some cases where the motion remained always continuous.

11. The general question of spherical sound-waves of finite amplitude is by no means an easy one. In the case of plane waves we can write down at once from Riemann's equations the condition that the disturbance may be propagated wholly in the positive or wholly in the negative direction. The respective conditions are* :—

$$u=\pm\int_{\rho_0}^{\rho}\sqrt{\frac{dp}{d\rho}}\,.\,d\log\rho,$$

where ρ_0 is the density of that part of the fluid whose velocity

* *Cf.* also Lord Rayleigh, 'Theory of Sound,' vol. ii. p. 35 (3).

is reckoned as zero. No such simple criterion can be given for the existence of a purely convergent or purely divergent spherical disturbance; a fact which may be readily seen from the equations for waves of infinitesimal amplitude. If ϕ is the potential of a purely divergent system of waves, we have

$$r\phi = f(at - r), \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where f is a function whose form is unrestricted. Let ρ be the ordinary density of the air, and $\rho + \delta\rho$ the actual density at a point where the coordinate is r and velocity u. We have, then, on differentiating (16) the well-known relations

$$u = \frac{\partial\phi}{\partial r} = -\frac{f(at-r)}{r^2} - \frac{f'(at-r)}{r} \quad . \quad . \quad . \quad (17)$$

and

$$a\frac{\delta\rho}{\rho} = -\frac{1}{a}\frac{\partial\phi}{\partial t} = -\frac{f'(at-r)}{r} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

From (17) and (18),

$$\left(a\frac{\delta\rho}{\rho} - u\right)r^2 = f(at-r),$$

whence differentiating with respect to r, and neglecting small quantities beyond the first order,

$$r^2\left(\frac{a}{\rho}\frac{\partial\rho}{\partial r} - \frac{\partial u}{\partial r}\right) + 2r\left(a\frac{\delta\rho}{\rho} - u\right) = -f'(at-r)$$
$$= ar\frac{\delta\rho}{\rho}$$

by (18); therefore

$$\frac{a}{\rho}\frac{\partial\rho}{\partial r} - \frac{2u}{r} + \frac{a}{r}\frac{\delta\rho}{\rho} - \frac{\partial u}{\partial r} = 0. \quad . \quad . \quad . \quad . \quad (19)$$

If, then, an infinitesimal spherical disturbance is to be purely divergent, this equation must be satisfied for every value of r. But since the left-hand side involves $\delta\rho/\rho$ as well as u, $\partial u/\partial r$, and $\partial(\log\rho)/\partial r$, it is evident that the question whether or not the equation is satisfied for some particular value of r does not depend solely on the state of things in the immediate neighbourhood of this value, but is influenced also by the value of ρ corresponding to the undisturbed air. We must not therefore seek to characterize a purely divergent disturbance by a differential equation expressing that, with respect to the air at each point, the disturbance is wholly propagated in the positive direction of r.

12. Not recognizing this, I had attempted to discover such an equation, and one step of the inquiry is reproduced here, for the sake of any interest which it may have.

It is required to write down the differential equation of an infinitesimal spherical disturbance, which is superposed on a purely radial steady motion.

Though a steady motion extending inward to the pole would involve a violation of the principle of continuity, we may suppose that throughout a shell of finite thickness the distribution of density and velocity is such as would be consistent with steady motion; the motion within such a shell would then continue steady, provided that its spherical boundaries were constrained to expand or contract in a suitable manner. In the absence of constraints the shell of steady motion would be invaded from without and from within by disturbances emanating from adjoining parts of the fluid, but, at points well within the shell, the character of the steady motion would necessarily be maintained for a finite time.

Let ϕ be the potential of the steady motion.

Let $\phi+\psi$ be the potential of the actual motion so that ψ and its derivatives are small.

Let p, ρ be the pressure and density in the steady motion.

Let $p+\delta p$, $\rho+\delta\rho$ be the pressure and density in the actual motion, and assume that the pressure is a function of the density only. From the ordinary equations for the motion of compressible fluids we obtain

$$\int^{p}\frac{dp}{\rho}=-\tfrac{1}{2}\left(\frac{\partial\phi}{\partial r}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\int^{p+\delta p}\frac{dp}{\rho}=-\tfrac{1}{2}\left(\frac{\partial\phi}{\partial r}+\frac{\partial\psi}{\partial r}\right)^2-\dot{\psi}$$

$$=-\tfrac{1}{2}\left(\frac{\partial\phi}{\partial r}\right)^2-\frac{\partial\phi}{\partial r}\frac{\partial\psi}{\partial r}-\dot{\psi}, \quad . \quad . \quad . \quad (21)$$

when small quantities of the second order are neglected. Subtracting (20) from (21)

$$\frac{\delta p}{\rho}=-\dot{\psi}-\frac{\partial\phi}{\partial r}\frac{\partial\psi}{\partial r}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now

$$\frac{\delta p}{\rho}=\frac{dp}{d\rho}\cdot\frac{\delta\rho}{\rho};$$

therefore

$$\frac{\partial}{\partial t}\frac{\delta p}{\rho}=\frac{dp}{d\rho}\cdot\frac{1}{\rho}\frac{\partial\,.\,\delta\rho}{\partial t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and the equations of continuity for the steady motion and the

actual motion may be written

$$0=\frac{\partial\rho}{\partial t}=-\rho\nabla^2\phi-\frac{\partial\phi}{\partial r}\frac{\partial\rho}{\partial r},$$

$$\frac{\partial(\rho+\delta\rho)}{\partial t}=-(\rho+\delta\rho)\nabla^2(\phi+\psi)-\left(\frac{\partial\phi}{\partial r}+\frac{\partial\psi}{\partial r}\right)\frac{\partial(\rho+\delta\rho)}{\partial r},$$

whence by subtraction

$$\frac{\partial\delta\rho}{\partial t}=-\rho\nabla^2\psi-\delta\rho\nabla^2\phi-\frac{\partial\rho}{\partial r}\frac{\partial\psi}{\partial r}-\frac{\partial\delta\rho}{\partial r}\frac{\partial\phi}{\partial r}. \quad . \quad (24)$$

Again,

$$\frac{\partial\delta\rho}{\partial r}=\frac{\partial}{\partial r}\left\{\left(\frac{dp}{d\rho}\right)^{-1}\delta p\right\}$$
$$=\frac{\partial}{\partial r}\left\{\rho\left(\frac{dp}{d\rho}\right)^{-1}\left(-\dot{\psi}-\frac{\partial\phi}{\partial r}\frac{\partial\psi}{\partial r}\right)\right\};$$

expanding this and substituting in (24) we get

$$\frac{\partial\delta\rho}{\partial t}=-\rho\nabla^2\psi-\rho\left(\frac{dp}{d\rho}\right)^{-1}\left(-\dot{\psi}-\frac{\partial\phi}{\partial r}\frac{\partial\psi}{\partial r}\right)\nabla^2\phi-\frac{\partial\rho}{\partial r}\frac{\partial\psi}{\partial r}$$
$$-\left[\frac{\partial}{\partial r}\left\{\rho\left(\frac{dp}{d\rho}\right)^{-1}\right\}\left(-\dot{\psi}-\frac{\partial\phi}{\partial r}\frac{\partial\psi}{\partial r}\right)\right.$$
$$\left.+\rho\left(\frac{dp}{d\rho}\right)^{-1}\left(-\frac{\partial\dot{\psi}}{\partial r}-\frac{\partial\phi}{\partial r}\frac{\partial^2\psi}{\partial r^2}-\frac{\partial^2\phi}{\partial r^2}\frac{\partial\psi}{\partial r}\right)\right]\frac{\partial\phi}{\partial r}. \quad (25)$$

Now differentiate (22) with respect to t and we have, remembering (23),

$$-\ddot{\psi}-\frac{\partial\phi}{\partial r}\frac{\partial\dot{\psi}}{\partial r}=\frac{1}{\rho}\frac{dp}{d\rho}\cdot\frac{\partial\delta\rho}{\partial t}.$$

In this equation we have to substitute the value of $\partial\delta\rho/\partial t$ from (25), and if we then put $\chi\equiv\psi r$, and perform the necessary reductions, we finally obtain as the differential equation satisfied by ψr,

$$\frac{\partial^2\chi}{\partial t^2}-(a^2-u^2)\frac{\partial^2\chi}{\partial r^2}+2u\frac{\partial^2\chi}{\partial r\partial t}+\mathrm{U}\frac{\partial\chi}{\partial t}+\mathrm{V}\left(\frac{\partial\chi}{\partial r}-\frac{\chi}{r}\right)=0,$$

where

$$a^2\equiv\text{the variable }\frac{dp}{d\rho}\text{ (in the steady motion)},$$

$$u\equiv\frac{\partial\phi}{\partial r}\equiv\frac{\text{constant}}{\rho r^2},$$

$$\mathrm{U}\equiv\frac{1}{\rho}\frac{\partial(u\rho)}{\partial r}-\frac{2u}{a}\frac{\partial a}{\partial r}\equiv-\frac{2u}{r}-\frac{2u}{a}\cdot\frac{\partial a}{\partial r},$$

$$\mathrm{V}\equiv 2au\frac{\partial}{\partial r}\left(\frac{u}{a}\right)-\frac{a^2-u^2}{\rho}\frac{\partial\rho}{\partial r}.$$

If the steady motion in question is a state of rest, $u=0$ and ρ is a constant, so that $U=0$, $V=0$, and our equation reduces to the ordinary form for small spherical disturbances,

$$\frac{\partial^2\chi}{\partial t^2}-a^2\frac{\partial^2\chi}{\partial r^2}=0.$$

If, on the other hand, $r=\infty$, the motion may, through any finite distance, be treated as linear. We shall then have u and ρ both constant, as well as a, and as before $U=0$, $V=0$. In that case

$$\frac{\partial^2\psi}{\partial t^2}-(a^2-u^2)\frac{\partial^2\psi}{\partial r^2}+2u\frac{\partial^2\psi}{\partial r\partial t}=0,$$

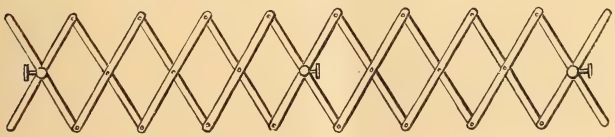
and this, by a change of independent variables, is easily seen to be the appropriate form for small plane disturbances of a fluid whose motion is otherwise uniform.

XXXIII. *On a new and handy Focometer.* *By* Professor J. D. Everett, *F.R.S.**

THIS focometer is designed to permit the distance of the "object" from the screen to be varied, while the lens which is to throw on the screen an image of the "object" is automatically kept midway between the two. This position, as is well known, gives both the sharpest definition and the simplest calculation.

The instrument is constructed on the principle of the well-known toy called *lazy-tongs*. A number of flat bars (fig. 1),

Fig. 1.



Plan.

all exactly alike, are jointed together in such a way that half of them are in one plane and the other half in a superposed plane. With the exception of the end bars, each bar in either plane is jointed to three of the bars in the other plane, one joint being in the middle and one at each end. The end bars are jointed at the middle and one end only. All the bars in the same plane are parallel, and the two sets together form a single row of rhombuses all equal and similar, a side of a rhombus being half the length of a bar. The system has only

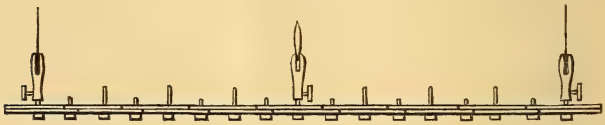
* Communicated by the Physical Society: read February 24, 1893.

one degree of freedom, and its length is a definite multiple of the longitudinal diagonal of a rhombus.

The joints are arranged in three rows, one down the middle and one along each edge, and the distance from joint to joint in any row is equal to this longitudinal diagonal. This common distance can be varied between very wide limits by pulling out or pushing in the frame, and we have thus a means of dividing an arbitrary length into any number of equal parts. I utilize only the middle row for this purpose, and utilize it only or chiefly for bisecting a variable distance.

The pins on which the middle joints turn are continued upwards, as shown in fig. 2, to serve as supports for clips holding the object, the lens, and the screen. The lens is

Fig. 2.



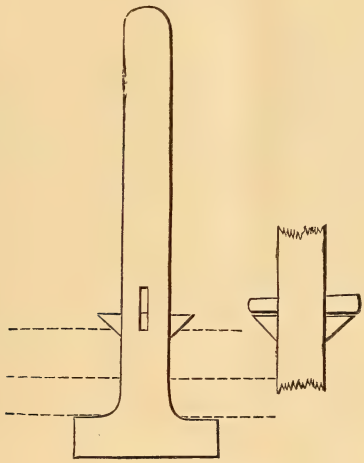
Elevation.

mounted on the centre pin, and the object and screen usually on the two end pins, as in fig. 2. In order to avoid flexibility, the clips are made short, and the pins, on which they are held by screws, rise only $1\frac{1}{2}$ inch above the frame. The base of each pin is a substantial disk (see fig. 3) which rests upon the table; all the pins, not only in the middle row, but also in the two outside rows, terminate in such disks, which serve as the feet of the instrument, and slide upon the table when the frame is expanded or contracted. The pins are of brass $\frac{1}{4}$ inch in diameter, and the bars are of $\frac{1}{4}$-inch mahogany, $\frac{3}{4}$ inch wide, and 13 inches in gross length. There are 18 of them, as shown in fig. 1. There are 9 pins in the middle row; and when the object and screen are on the two end pins, the distance between them is divided by the other pins into 8 equal parts, any two of which should together make up the focal length. The unused pins are the most convenient handles for manipulating the frame.

The screen may conveniently be a piece of white card a little larger than a post-card, and a square of wire-gauze about half as big may be used as the object; but a still better 'object' is a cross of threads stretched across a square hole in a card. The light which passes through the square hole is very conspicuous on the screen before the correct distance is approached, whereas the shadow of the wire

gauze is almost invisible. Two thin cards about the size of post-cards should be taken, a hole a centimetre square should be cut through both of them, and they should be gummed together with the cross threads between them, the threads being in the first instance long enough to project beyond the cards to facilitate adjustment while the gum is wet. Waxed carpet-thread, or any very stout thread with smooth edges, is

Fig. 3.



A supporting pin.

the best for giving a conspicuous and at the same time a sharp image. As the cross will sometimes have to be raised or lowered, the hole should be much nearer to one end of the card than to the other, in order to give a greater range of adjustment in mounting on the clip. One thread should be vertical and the other horizontal, in order that their simultaneous focussing may serve as a check on the correct orientation of the lens.

The instrument is intended to be used by placing it on a table of length not less than four times the focal distance which is to be measured. A lamp is to be placed either on one end of the table or on a stand opposite the end, at such a height that its flame is about level with the tops of the clips. The clips should be fixed as low as possible on their supporting pins, unless it is necessary to raise them to suit the height of the lamp. In default of a lamp at the proper height, an adjustable mirror may be used instead, and made to reflect a beam of light from any large gas-flame in the room so that the beam shall pass along the tops of the clips.

When the lamp or mirror has once been adjusted to throw its light in the proper direction, it should not be disturbed, as all necessary adjustments can be better made by moving the instrument.

The lens and screen may conveniently be mounted first, and the adjustments made so that the light collected by the lens falls on the screen as a horizontal beam. The cross is then to be mounted in such a position that a bright patch corresponding to the square hole is seen on the screen, surrounded by the shadow of the card. The frame must now be extended or compressed till the image of the cross appears in the bright patch; and the lens, object, and screen should then be carefully set square by hand before the final adjustment. If the vertical and horizontal lines of the cross do not focus simultaneously, it is a sign that the lens needs setting square.

The focussing having been completed, the distance of the object from the image is to be measured and divided by four. This will give the focal length; and the calculation can be checked by measuring one or more of the four equal parts into which the distance is divided by alternate pins. Owing to slight play in some of the joints, or other mechanical imperfections, the theoretically equal distances may exhibit sensible differences, especially when the frame is nearly closed up; but the method of observation is so well conditioned that these inequalities do not practically affect the correctness of the result.

In fact, if the distances of the lens from the object and image, instead of being exactly equal, are $a+x$ and $a-x$, the true focal length is $\frac{a^2-x^2}{2a}$, and in taking it to be one fourth of the whole distance we are simply neglecting x^2 in comparison with a^2. Suppose the two distances $a+x$ and $a-x$ to measure $20\frac{1}{2}$ and $19\frac{1}{2}$ inches, which is a larger inequality than is likely to occur, the ratio of x^2 to a^2 is 1 to 1600; and this error is negligible, in view of the fact that the doubt as to when the image is sharpest involves an uncertainty in the focal length to the extent usually of more than one per cent.

When the focal length does not exceed 10 or 12 inches, the instrument may be supported with the two hands and pointed towards a gas-flame, which need not be at the same level, but may be at any height. A fairly good measurement can thus be made by one person, if there is opportunity for setting the instrument down on a table or floor when the lens needs setting square, and when the final measurement of distance is to be made. The friction at the joints of the

frame is just sufficient to keep them from working while the instrument is being carefully set down. The chief difficulty is from flexure.

Instead of receiving the image on a screen, it can be viewed in mid air. For this purpose I mount the cross on one of the two end clips, and a piece of wire gauze about the size of the palm of my hand on the other, setting the wires at a slope of 45° by way of contrast with the upright cross. The end which carries the cross should be turned towards the strongest light; as this renders the cross more visible to an observer behind the gauze, and also renders the glistening wires of the gauze more visible when the observer stations himself behind the cross. The adjustment for focus is made by lengthening or shortening the frame till parallax is removed. This is a very convenient way of establishing experimentally the fact of the interchangeableness of object and image.

The instrument can also be employed to illustrate the general law of variation of conjugate focal distances, the lens being for this purpose shifted from the central pin to any one of the other pins, and the frame being then extended till the image is correctly focussed. Regarded as an optical bench, the instrument is remarkably light and handy. Its weight, including screen, cross, wire-gauze, and lens, is 2 lb. 10 oz.; and a lecturer can carry it through the streets of a town without inconvenience.

The dimensions and number of bars of the instrument as exhibited are recommended as the most convenient for general purposes. Ten bars only were constructed for the first trials, and any number included in the formula $4n+2$ might theoretically be employed.

In order to prevent looseness at the joints, it would be well to make the holes in the bars bear against a cone below and another cone above, with a very slightly tapering wedge for adjustment, as indicated in fig. 3.

If the instrument were to be set up permanently in one place, guides might be used for compelling the middle row of pins to travel without rotation, or the pin on which the lens is mounted might be a fixture; but as long as portability is to be preserved, I do not think that any arrangements for automatically preventing rotation would be practically beneficial. It is only in the large movements which precede the final adjustment that rotation occurs to any injurious extent.

The instrument has been constructed from my drawings by Messrs. Yeates of Dublin, and the cost is trifling.

XXXIV. *A Hydrodynamical Proof of the Equations of Motion of a Perforated Solid, with Applications to the Motion of a Fine Rigid Framework in Circulating Liquid.* By G. H. Bryan*.

Introduction.

1. In the whole range of hydrodynamics, there is probably no investigation which presents so many difficulties as that which deals with the equations of motion of a perforated solid in liquid. The object of the present paper is to show how these equations may be deduced directly from the pressure-equation of hydrodynamics, without having recourse to the laborious method of ignoration of coordinates. The possibility of doing this is mentioned by Prof. Lamb in his 'Treatise on the Motion of Fluids' (pp. 119, 120), but he dismisses the method with the brief remark that in most cases it would prove exceedingly tedious. I think, however, that it will be admitted that the following investigation is more straightforward and simple than that given by Basset in his 'Hydrodynamics,' vol. i. pp. 167–178.

The usual method presents little difficulty when the motion of the liquid is acyclic, because the whole motion could in such cases be set up from rest by suitable impulses applied to the solids alone; and a consideration of Routh's modified Lagrangian function shows that in this case the equations of motion can be obtained by expressing the total kinetic energy as a quadratic function of the velocity-components of the solid alone, and applying the generalized equations of motion referred to moving axes.

If, however, the solid is perforated, and the liquid is circulating through the perforations, this method presents several difficulties. If the solid were reduced to rest by the application of suitable impulses, the liquid would still continue to circulate through the perforations, the "circulation" in any circuit remaining unaltered. From this and other circumstances we are led to infer that these circulations are not generalized velocity-components, but rather that the quantities $\kappa\rho$ are generalized momenta. Now the kinetic energy of the system is naturally calculated as a function of the velocity-components of the solid and of these constant circulations (or the corresponding momenta); a form unsuited for obtaining the equations of motion. We ought either to have the kinetic energy expressed in terms of generalized velocity-components alone, or to know the "modified Lagrangian

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function" obtained by "ignoring" the velocity-components corresponding to the constant momenta or circulations. Either of these expressions involves constants which cannot be determined from the ordinary expression for the energy alone, and to determine them in the usual way it is necessary to resort to arguments based on a consideration of the "impulse" by which the motion might be set up from rest.

In the following investigation the equations of motion are deduced from purely hydrodynamical considerations, and from them the modified function is found. In §§ 12–16 the equations of motion are interpreted for the case in which the solid is a light rigid framework and the inertia is entirely due to the circulation of the liquid, and the results are applied to interpret the effective forces of the cyclic motion for a perforated solid in general.

General Hydrodynamical Equations.

2. Let a perforated solid bounded by the surface S be moving through an infinite mass of liquid (density ρ) with translational and rotational velocity-components u, v, w, p, q, r, referred to axes fixed in the solid, and let $\kappa_1, \kappa_2, \kappa_3 \ldots \kappa_m$ be the circulations in circuits drawn through the various apertures. Then we know that ϕ the velocity-potential of the fluid motion may be expressed as a linear function of the velocities and circulations in the form

$$\phi = u\phi_u + v\phi_v + w\phi_w + p\phi_p + q\phi_q + r\phi_r + \Sigma\kappa\phi_\kappa, \quad . \quad (1)$$

where evidently $\phi_u = \partial\phi/\partial u$ &c., and the coefficients $\phi_u \ldots$ depend only on the form of the solid.

If $d\nu$ denotes the element of the normal to S measured from the solid into the liquid, (l, m, n) its direction-cosines, then, in the usual way, we have

$$\frac{\partial\phi}{\partial\nu} = l(u - ry + qz) + m(v - pz + rx) + n(w - qx + py). \quad . \quad (2)$$

The six coefficients $\phi_u \ldots \phi_r$ are single-valued functions of the coordinates, while the coefficients ϕ_κ which determine the part of the velocity-potential due to the circulations are cyclic functions making $\partial\phi_\kappa/\partial\nu = 0$ at the surface of the solid; these coefficients are supposed known for each form of solid, although their determination in any given case is generally beyond the range of mathematical analysis.

3. Let $\sigma_1, \sigma_2, \ldots \sigma_m$ be barriers drawn across the perforations; then, in the usual way, the kinetic energy of the liquid

is found to be $\mathfrak{T}$, where

$$\mathfrak{T} = -\tfrac{1}{2}\rho \iint \phi \frac{\partial \phi}{\partial \nu}\, dS + \tfrac{1}{2}\rho \Sigma \kappa \iint \frac{\partial \phi}{\partial \nu}\, d\sigma = \mathfrak{T}_1 + K. \quad . \quad (3)$$

Here $\mathfrak{T}_1$ is a quadratic function of the velocity-components of the solid, and is the kinetic energy when the motion is acyclic, and K is a quadratic function of the circulations.

If the axes were fixed in space, the pressure equation (supposing no forces to act on the liquid) would be

$$\frac{p_1}{\rho} + \frac{\partial \phi}{\partial t} + \tfrac{1}{2} q_1^2 = \text{const.},$$

(where p_1 = pressure, q_1 = resultant velocity of liquid). Owing to the motion of the axes, however, $\partial\phi/\partial t$ must be replaced by the rate of change of ϕ at a fixed point, that is by

$$\frac{d\phi}{dt} - (u - yr + zq)\frac{\partial \phi}{\partial x} - (v - zp + xr)\frac{\partial \phi}{\partial y} - (w - xq + yp)\frac{\partial \phi}{\partial z},$$

whence the pressure equation becomes

$$\frac{p_1}{\rho} + \frac{d\phi}{dt} - (u - yr + zq)\frac{\partial \phi}{\partial x} - (v - zp + xr)\frac{\partial \phi}{\partial y} - (w - xq + yp)\frac{\partial \phi}{\partial z} + \tfrac{1}{2} q_1^2 = \text{const.} \quad . \quad . \quad . \quad . \quad (4)$$

The Mutual Reactions between the Solid and Liquid.

4. Let X_1, Y_1, Z_1, L_1, M_1, N_1 be the component forces and couples which the solid exerts on the liquid; then we have evidently

$$X_1 = \iint l\, p_1\, dS, \quad L_1 = \iint (ny - mz)\, p_1\, dS. \quad . \quad . \quad (5)$$

To reduce these expressions to the required form, we shall have to resort to repeated applications of Green's formula. Since the velocity-potential ϕ is a multiple-valued function, it follows that in transforming volume integrals involving ϕ we shall obtain surface integrals over the barriers $\sigma_1, \sigma_2, \ldots \sigma_m$ as well as over S the surface of the solid. On the other hand, the pressure p_1 and the velocity-components $\partial\phi/\partial x$, $\partial\phi/\partial y$, $\partial\phi/\partial z$ are single-valued and do not contribute barrier terms to the surface integrals. Moreover, since the circulations κ are independent of the time,

$$\frac{\partial \phi}{\partial t} = u\phi_u + \dot{v}\phi_v + \dot{w}\phi_w + \dot{p}\phi_p + \dot{q}\phi_q + \dot{r}\phi_r;$$

and $\partial\phi/\partial t$ is therefore a single-valued function of the velocity-components of the solid satisfying Laplace's equation.

We also notice that

$$l = \frac{\partial \phi_u}{\partial \nu}, \quad ny - mz = \frac{\partial \phi_p}{\partial \nu}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as may be at once seen by differentiating (2) with respect to u and p respectively.

5. Substituting for p_1 in (5) in terms of the velocities, we have

$$\frac{X}{\rho} = -\iint l \frac{d\phi}{dt} dS$$

$$+ \iint \left\{ (u - yr + zq) \frac{\partial \phi}{\partial x} + (\text{two similar}) \right\} l dS$$

$$- \tfrac{1}{2} \iint \left\{ \left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 \right\} l dS. \quad . \quad . \quad . \quad . \quad (7)$$

The first line of this expression is, from (6), equal to

$$- \iint \frac{d\phi}{dt} \frac{\partial \phi_u}{\partial \nu} dS$$

$$= \iiint \left\{ \frac{\partial \dot{\phi}}{\partial x} \frac{\partial \phi_u}{\partial x} + \frac{\partial \dot{\phi}}{\partial y} \frac{\partial \phi_u}{\partial y} + \frac{\partial \dot{\phi}}{\partial z} \frac{\partial \phi_u}{\partial z} \right\} dx\, dy\, dz$$

by Green's transformation. Remembering that ϕ_u is independent of the time, this integral, taken throughout the liquid, becomes

$$= \frac{d}{dt} \frac{\partial}{\partial u} \tfrac{1}{2} \iiint \left\{ \left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 \right\} dx\, dy\, dz$$

$$= \frac{1}{\rho} \frac{d}{dt} \frac{\partial \mathfrak{T}}{\partial u} = \frac{1}{\rho} \frac{\partial}{\partial t} \frac{\partial \mathfrak{T}_1}{\partial u}.$$

By Green's transformation the second line is equal to

$$- \iiint \frac{\partial}{\partial x} \left\{ (u - yr + zq) \frac{\partial \phi}{\partial x} + (\text{two similar}) \right\} dx\, dy\, dz$$

$$= - \iiint \left(r \frac{\partial \phi}{\partial y} - q \frac{\partial \phi}{\partial z} \right) dx\, dy\, dz$$

$$- \iiint \left\{ (u - yr + zq) \frac{\partial}{\partial x} + (\text{two similar}) \right\} \frac{\partial \phi}{\partial x} dx\, dy\, dz,$$

which by a second application of Green's transformation becomes

$$=\iint(mr-nq)\phi dS-\Sigma\kappa\iint(mr-nq)d\sigma$$
$$+\iint\{l(u-yr+zq)+m(v-zp+xr)+n(w-xq+yp)\}\frac{\partial\phi}{\partial x}dS$$
$$=\iint(mr-nq)\phi dS-\Sigma\kappa\iint(mr-nq)d\sigma+\iint\frac{\partial\phi}{\partial\nu}\frac{\partial\phi}{\partial x}dS$$

by (2).

Lastly, the third line of (7) is, by Green's transformation,

$$=\iiint\left\{\frac{\partial\phi}{\partial x}\frac{\partial^2\phi}{\partial x^2}+\frac{\partial\phi}{\partial y}\frac{\partial^2\phi}{\partial x\partial y}+\frac{\partial\phi}{\partial z}\frac{\partial^2\phi}{\partial x\partial z}\right\}dx\,dy\,dz$$
$$=-\iint\frac{\partial\phi}{\partial\nu}\frac{\partial\phi}{\partial x}dS.$$

Hence, adding the several terms together, we have

$$X_1=\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u}$$
$$+r\{\rho\iint m\phi dS-\Sigma\kappa\rho\iint md\sigma\}-q\{\rho\iint n\phi dS-\Sigma\kappa\rho\iint nd\sigma\}\ . \quad (8)$$

Now by (6),

$$\rho\iint m\phi dS=\rho\iint\frac{\partial\phi_v}{\partial\nu}\phi dS$$
$$=\Sigma\kappa\rho\iint\frac{\partial\phi_v}{\partial\nu}d\sigma-\rho\iiint\left\{\frac{\partial\phi}{\partial x}\frac{\partial\phi_v}{\partial x}+\frac{\partial\phi}{\partial y}\frac{\partial\phi_v}{\partial y}+\frac{\partial\phi}{\partial z}\frac{\partial\phi_v}{\partial z}\right\}dx\,dy\,dz$$
$$=\Sigma\kappa\rho\iint\frac{\partial\phi_v}{\partial\nu}d\sigma-\frac{\partial}{\partial v}\tfrac{1}{2}\rho\iiint\left\{\left(\frac{\partial\phi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial z}\right)^2\right\}dx\,dy\,dz$$
$$=\Sigma\kappa\rho\iint\frac{\partial\phi_v}{\partial\nu}d\sigma-\frac{\partial\mathfrak{T}}{dv}.$$

Therefore

$$X_1=\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u}-r\left\{\frac{\partial\mathfrak{T}}{\partial v}+\Sigma\kappa\rho\iint\left(m-\frac{\partial\phi_v}{\partial\nu}\right)d\sigma\right\}$$
$$+q\left\{\frac{\partial\mathfrak{T}}{\partial w}+\Sigma\kappa\rho\iint\left(n-\frac{\partial\phi_w}{\partial\nu}\right)d\sigma\right\}\ .\ .\ .\ (9)$$

6. In like manner we have

$$\frac{L_1}{\rho}=-\iint(ny-mz)\frac{d\phi}{dt}dS$$
$$+\iint\left\{(u-yr+zq)\frac{\partial\phi}{\partial x}+(\text{two similar})\right\}(ny-mz)dS$$

$$-\tfrac{1}{2}\iint\left\{\left(\frac{\partial\phi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial z}\right)^2\right\}(ny-mz)\,dS$$

$$=-\iint\frac{d\phi}{dt}\frac{\partial\phi_p}{\partial\nu}\,dS$$

$$-\iiint\left\{y\left(q\frac{\partial\phi}{\partial x}-p\frac{\partial\phi}{\partial y}\right)-z\left(p\frac{\partial\phi}{\partial z}-r\frac{\partial\phi}{\partial x}\right)\right\}dx\,dy\,dz$$

$$-\iiint\left[y\left\{(u-yr+zq)\frac{\partial}{\partial x}+(\text{two similar})\right\}\frac{\partial\phi}{\partial z}\right.$$

$$\left.-z\left\{(u-yr+zq)\frac{\partial}{\partial x}+(\text{two similar})\right\}\frac{\partial\phi}{\partial y}\right]dx\,dy\,dz$$

$$+\iiint\left(\frac{\partial\phi}{\partial x}\frac{\partial}{\partial x}+\frac{\partial\phi}{\partial y}\frac{\partial}{\partial y}+\frac{\partial\phi}{\partial z}\frac{\partial}{\partial z}\right)\left(y\frac{\partial\phi}{\partial z}-z\frac{\partial\phi}{\partial y}\right)dx\,dy\,dz$$

$$=\frac{1}{\rho}\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial p}$$

$$+\iint\left\{l(u-yr+zq)+(\text{two sim.})-\frac{\partial\phi}{\partial\nu}\right\}\left(y\frac{\partial\phi}{\partial z}-z\frac{\partial\phi}{\partial y}\right)dS$$

$$-\iiint\left[y\left(q\frac{\partial\phi}{\partial x}-p\frac{\partial\phi}{\partial y}\right)-z\left(p\frac{\partial\phi}{\partial z}-r\frac{\partial\phi}{\partial x}\right)\right.$$

$$\left.-(v-zp+xr)\frac{\partial\phi}{\partial z}+(w-xq+yp)\frac{\partial\phi}{\partial y}\right]dx\,dy\,dz.$$

Remembering that in this expression one factor of the surface integral is zero at every point of S, we have, by again applying Green's transformation to the volume integral,

$$\begin{aligned}L_1=&\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial p}\\&+w\{\rho\iint m\phi\,dS-\Sigma\kappa\rho\iint m\,d\sigma\}-v\{\rho\iint n\phi\,dS-\Sigma\kappa\rho\iint n\,d\sigma\}\\&+r\{\rho\iint(lz-nx)\phi\,dS-\Sigma\kappa\rho\iint(lz-nx)\,d\sigma\}\\&-q\{\rho\iint(mx-ly)\phi\,dS-\Sigma\kappa\rho\iint(mx-ly)\,d\sigma\}\quad.\quad.\quad(10)\end{aligned}$$

Now, just as before,

$$\begin{aligned}\rho\iint(lz-mx)\phi\,dS&=\rho\iint\frac{\partial\phi_q}{\partial\nu}\phi\,dS\\&=\Sigma\kappa\rho\iint\frac{\partial\phi_q}{\partial\nu}\,d\sigma\\&\qquad-\rho\iiint\left(\frac{\partial\phi}{\partial x}\frac{\partial\phi_q}{\partial x}+\frac{\partial\phi}{\partial y}\frac{\partial\phi_q}{\partial y}+\frac{\partial\phi}{\partial z}\frac{\partial\phi_q}{\partial z}\right)dx\,dy\,dz\\&=\Sigma\kappa\rho\iint\frac{\partial\phi_q}{\partial\nu}\,d\sigma-\frac{\partial\mathfrak{T}}{\partial q}.\end{aligned}$$

Therefore,

$$
\begin{aligned}
L_1 = \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial p} & \\
& -w\left\{\frac{\partial \mathfrak{T}}{\partial v} + \Sigma\kappa\rho\iint\left(m - \frac{\partial \phi_v}{\partial \nu}\right)d\sigma\right\} \\
& +v\left\{\frac{\partial \mathfrak{T}}{\partial w} + \Sigma\kappa\rho\iint\left(n - \frac{\partial \phi_w}{\partial \nu}\right)d\sigma\right\} \\
& -r\left\{\frac{\partial \mathfrak{T}}{\partial q} + \Sigma\kappa\rho\iint\left(lz - nx - \frac{\partial \phi_q}{\partial \nu}\right)d\sigma\right\} \\
& +q\left\{\frac{\partial \mathfrak{T}}{\partial r} + \Sigma\kappa\rho\iint\left(mx - ly - \frac{\partial \phi_r}{\partial \nu}\right)d\sigma\right\}. \quad . \quad (11)
\end{aligned}
$$

Application to the Equations of Motion.

7. The equations of motion of the solid may now be written down at once. Let $\mathfrak{T}'$ be the kinetic energy of the solid, T the total kinetic energy $=\mathfrak{T}+\mathfrak{T}'$; and suppose that the motion takes place under the action of a system of external impressed forces and couples designated by X, Y, Z, L, M, N. Then the effective forces and couples to which the motion of the solid itself is due are $X-X_1\ldots$, $L-L_1\ldots$, respectively, and the six equations of motion of the solid referred to the moving axes are of the form

$$\frac{d}{dt}\frac{\partial \mathfrak{T}'}{\partial u} - r\frac{\partial \mathfrak{T}'}{\partial v} + q\frac{\partial \mathfrak{T}'}{\partial w} = X - X_1, \quad . \quad . \quad . \quad (12)$$

$$\frac{d}{dt}\frac{\partial \mathfrak{T}'}{\partial p} - w\frac{\partial \mathfrak{T}'}{\partial v} + v\frac{\partial \mathfrak{T}'}{\partial w} - r\frac{\partial \mathfrak{T}'}{\partial q} + q\frac{\partial \mathfrak{T}'}{\partial r} = L - L_1. \quad . \quad (13)$$

Hence, on substitution, we see that the required equations of motion are found by writing T for $\mathfrak{T}$ and X, Y, Z, L, M, N for $X_1, Y_1, Z_1, L_1, M_1, N_1$ in equations (9) (11). The resulting equations may be written :

$$X = \frac{d}{dt}\frac{\partial T}{\partial u} - r\left(\frac{\partial T}{\partial v} + \eta\right) + q\left(\frac{\partial T}{\partial w} + \zeta\right), \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$
\begin{aligned}
L = \frac{d}{dt}\frac{\partial T}{\partial p} - w\left(\frac{\partial T}{\partial v} + \eta\right) + v\left(\frac{\partial T}{\partial w} + \zeta\right) & \\
& -r\left(\frac{\partial T}{\partial q} + \mu\right) + q\left(\frac{\partial T}{\partial r} + \nu\right), \quad (15)
\end{aligned}
$$

where ξ, η, ζ, λ, μ, ν are defined by the equations

$$\xi = \Sigma\kappa\rho\iint\left(l - \frac{\partial\phi_u}{\partial\nu}\right)d\sigma, \text{ \&c.} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\lambda = \Sigma\kappa\rho\iint\left(ny - mz - \frac{\partial\phi_p}{\partial\nu}\right)d\sigma, \text{ \&c.} \quad . \quad . \quad . \quad (17)$$

As Lamb has pointed out ('Motion of Fluids,' p. 140), the six quantities (ξ, η, ζ, λ, μ, ν) are "the components of the impulse of the cyclic fluid motion which remains when the solid is (by forces applied to it alone) brought to rest"*. They are linear functions of the circulations and their form depends on the form of the solid. If there is only one aperture they are all proportional to the circulation κ.

The Modified Lagrangian Function.

8. We shall now show that the motion of the solid can be determined in terms of Routh's modified Lagrangian function, and shall find the form of this function for the system. Putting

$$\mathrm{H} = \mathrm{T} + \xi u + \eta v + \zeta w + \lambda p + \mu q + \nu r + \mathrm{F}(\kappa\rho), \quad . \quad . \quad (18)$$

where $\mathrm{F}(\kappa\rho)$ denotes any function whatever of the quantities $\kappa\rho$, we see that the equations of motion reduce to the standard form

$$\mathrm{X} = \frac{d}{dt}\frac{\partial \mathrm{H}}{\partial u} - r\frac{\partial \mathrm{H}}{\partial v} + q\frac{\partial \mathrm{H}}{\partial w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$\mathrm{L} = \frac{d}{dt}\frac{\partial \mathrm{H}}{\partial p} - w\frac{\partial \mathrm{H}}{\partial v} + v\frac{\partial \mathrm{H}}{\partial w} - r\frac{\partial \mathrm{H}}{\partial q} + q\frac{\partial \mathrm{H}}{\partial r}. \quad . \quad (20)$$

The function H, therefore, plays the same part in determining the equations of motion of the solid as the kinetic energy T in the case of an imperforated solid (or any solid when the motion of the liquid is acyclic). It remains (i.) to determine what quantities are to be regarded as the generalized velocities if the quantities $\kappa\rho$ are regarded as generalized momenta; (ii.) to find the form of the function $\mathrm{F}(\kappa\rho)$ in order that H may represent the modified Lagrangian function.

9. Let $\dot{\chi}_m$ be the generalized velocity-component corresponding to the ignored momentum $\kappa_m\rho$. Then, as Routh has shown ('Rigid Dynamics,' vol. i. § 420), the modified Lagrangian function H is of the form

$$\mathrm{H} = \mathrm{T} - \Sigma\kappa_m\rho\dot{\chi}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

* Our ξ, η, ζ, λ, μ, ν are the same as the ξ_0, η_0, ζ_0, λ_0, μ_0, ν_0 of Lamb, or the $\mathfrak{X}$, $\mathfrak{Y}$, $\mathfrak{Z}$, $\mathfrak{L}$, $\mathfrak{M}$, $\mathfrak{N}$ of Basset's 'Hydrodynamics.'

and therefore by equating the two expressions for H we must have

$$\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r+\mathrm{F}(\kappa)=-\Sigma\kappa\rho\dot{\chi}. \quad . \quad . \quad (22)$$

Since $\dot{\chi}_m$ is the generalized velocity-component corresponding to the momentum $\kappa_m\rho$, therefore

$$\frac{\partial \mathrm{H}}{\partial\,.\,\kappa_m\rho}=-\dot{\chi}_m. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Now H is a homogeneous quadratic function of the six velocities $(u\ldots,p\ldots)$ and the momenta $\kappa\rho$; therefore

$$2\mathrm{H}=\Sigma u\frac{\partial \mathrm{H}}{\partial u}+\Sigma\kappa\rho\frac{\partial \mathrm{H}}{\partial\,.\,\kappa\rho}=\Sigma u\frac{\partial \mathrm{H}}{\partial u}-\Sigma\kappa\rho\dot{\chi}. \quad . \quad (24)$$

Hence, from (21),

$$2\mathrm{T}=\Sigma u\frac{\partial \mathrm{H}}{\partial u}+\Sigma\kappa\rho\dot{\chi}=\Sigma u\frac{\partial \mathrm{H}}{\partial u}-\Sigma\kappa\rho\frac{\partial \mathrm{H}}{\partial\,.\,\kappa\rho}. \quad . \quad . \quad (25)$$

The portions of T and H which involve only the momenta $\kappa\rho$, and are independent of the six velocities $(u\ldots,p\ldots)$, must arise from the terms $\Sigma\kappa\rho\dot{\chi}$ in the above expressions (24) (25), and must therefore be equal and of opposite sign in the expressions T and H respectively. Hence, since from (3)

$$\mathrm{T}=\mathfrak{T}'+\mathfrak{T}_1+\mathrm{K},$$

the portion of H which is independent of the six velocities $(u\ldots,p\ldots)$ must be $-\mathrm{K}$, so that

$$\begin{aligned}\mathrm{H}&=\mathfrak{T}'+\mathfrak{T}_1+(\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r)-\mathrm{K}\\ &=\mathrm{T}+(\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r)-2\mathrm{K}, \quad . \quad . \quad (26)\end{aligned}$$

and therefore $$\mathrm{F}(\kappa\rho)=-2\mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The function $\mathrm{F}(\kappa\rho)$ does not enter into the six equations of motion of the solid, but its form requires to be determined if we wish to reduce the equations of motion of the whole system to the canonical or Hamiltonian form.

The Generalized Velocities and Momenta.

10. Comparing (21) with (27), we see that

$$\Sigma\kappa\rho\dot{\chi}=2\mathrm{K}-(\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r). \quad . \quad (28)$$

Now equation (3) may be written in the form

$$\begin{aligned}2(\mathfrak{T}_1+\mathrm{K})=&-\rho\iint\phi\frac{\partial}{\partial\nu}(u\phi_u+\ldots+p\phi_p+\ldots+\Sigma\kappa\phi_\kappa)d\mathrm{S}\\ &+\Sigma\kappa\rho\iint\frac{\partial}{\partial\nu}(u\phi_u+\ldots+p\phi_p+\ldots+\Sigma\kappa\phi_\kappa)d\sigma. \quad (29)\end{aligned}$$

But by § 2, $\partial\phi_\kappa/\partial\nu=0$ all over the surface S of the solid. Hence, equating the terms independent of the six velocities $(u\ldots,p\ldots)$ on the two sides of (29), we have

$$2\mathrm{K}=\Sigma\kappa\rho\iint\frac{\partial}{\partial\nu}(\Sigma\kappa\phi_\kappa)d\sigma. \quad . \quad . \quad . \quad . \quad (30)$$

But by (16) (17),

$$\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r$$
$$=-\Sigma\kappa\rho\iint\frac{\partial}{\partial\nu}(u\phi_u+\ldots+p\phi_p+\ldots)d\sigma$$
$$+\Sigma\kappa\rho\iint\{lu+mv+nw+(ny-mz)p+\ldots\}d\sigma.$$

Hence, by (28) and (30),

$$\Sigma\kappa\rho\dot{\chi}=\Sigma\kappa\rho\iint\frac{\partial}{\partial\nu}(u\phi_u+\ldots+p\phi_p+\ldots+\Sigma\kappa\phi_\kappa)d\sigma$$
$$-\Sigma\kappa\rho\iint\{l(u-yr+zq)+m(v-zp+xr)+n(w-xq+yp)\}d\sigma;$$

and therefore

$$\dot{\chi}_m=\iint\left(\frac{\partial\phi}{\partial\nu}-l(u-yr+zq)-(\text{two similar})\right)d\sigma_m. \quad . \quad (31)$$

Now $\partial\phi/\partial\nu$ is the velocity of the liquid resolved along the normal to the barrier σ_m, and

$$l(u-yr+zq)+m(v-zp+xr)+n(w-xq+yp)$$

is the velocity of the barrier σ_m resolved normally to itself at the point x, y, z, supposing the barrier to be fixed relatively to the solid. Their difference, therefore, represents the normal relative velocity of the liquid with respect to the barrier.

Hence $\dot{\chi}_m$ represents the total rate of flow of the liquid across the barrier σ_m relative to the solid; in other words, the generalized velocity corresponding to the ignored momentum $\rho\kappa_m$ is the volume of liquid per unit time flowing through the aperture relatively to the solid.

This property is proved in a different way by Basset in his 'Hydrodynamics,' vol. i. page 176.

The Form of the Modified Function.

11. It may be interesting to examine a little more closely the effect of the circulations on the motion of a solid.

When the motion of the liquid is acyclic, the kinetic energy is a homogeneous quadratic function of (u, v, w, p, q, r). In general it therefore involves 21 constants, but by a suitable

choice of axes it is *always* possible to reduce this number by six, and a further reduction may be effected when the body is symmetrical. When the motion is cyclic the kinetic energy must be replaced by the modified function which in addition contains the seven terms

$$\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r-\mathrm{K},$$

of which the last term does not enter into the equations of motion of the solid. The six coefficients $(\xi, \ldots \lambda, \ldots)$ are linear functions of the circulations, and they remain constant so long as only conservative forces act on the liquid, for the circulations themselves then remain constant. Hence the modified function H may be regarded as a non-homogeneous quadratic function of the six velocities involving 28 constants, of which 27 enter into the six equations of motion of the solid.

Equations of Motion of a light thin framework of rigid wires.

12. To take the simplest possible case, let us suppose the solid to consist of a network of infinitely thin rigid massless wires through the meshes of which the liquid is circulating. If the motion of the liquid were acyclic, the wires would simply cut through the liquid without setting it in motion: hence the kinetic energy $\mathfrak{T}'+\mathfrak{T}_1$ of the acyclic motion vanishes, and the modified function becomes

$$\mathrm{H}=\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r-\mathrm{K}, \quad . \quad . \quad (32)$$

a result otherwise evident from the fact that $\mathfrak{T}_1$ only involves surface integrals taken over the infinitely small surface of the solid, while $\xi, \eta, \zeta, \lambda, \mu, \nu$ being integrals taken over the finite surfaces of barriers are in general finite.

If we choose as our axis of x the Poinsot's central axis of the impulse whose six components are $\xi, \eta, \zeta, \lambda, \mu, \nu$, the modified function will reduce to the form

$$\mathrm{H}=\Xi u+\Lambda p-\mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

If there is only one aperture, $\xi, \eta, \zeta, \lambda, \mu, \nu$ are all proportional to the circulation κ and the central axis of the impulse is fixed in position relative to the solid: if there are several apertures the position of the axis depends on the ratios of the circulations through the various apertures, but throughout the motion it in every case remains fixed relatively to the solid.

The six equations of motion (19) (20) now reduce to

$$\left.\begin{array}{ll} \mathrm{X}=0, & \mathrm{L}=0, \\ \mathrm{Y}=r\Xi, & \mathrm{M}=w\Xi+r\Lambda, \\ \mathrm{Z}=-q\Xi, & \mathrm{N}=-v\Xi-q\Lambda. \end{array}\right\} \quad . \quad . \quad . \quad (34)$$

Since these equations do not involve u or p, we see that *no forces will have to act on the solid in order to maintain a screw motion whose axis coincides with the central axis of the impulse.*

13. To interpret the equations still further, let us suppose that u and p are both zero, since they do not enter into the equations of motion. Then the motion whose components are $(0, v, w, 0, q, r)$ consists of two screws whose axes are the axes of y and z respectively, and, by the theory of screws, these are equivalent to a single screw whose axis is a certain straight line intersecting the axis of x and perpendicular to it. We may take this straight line as our axis of z, for hitherto we have only fixed the position of the axis of x. We have then

$$v=0, \quad q=0.$$

The equations (34) therefore reduce to

$$\left.\begin{array}{ll} X=0, & L=0, \\ Y=r\Xi, & M=w\Xi+r\Lambda, \\ Z=0, & N=0. \end{array}\right\} \quad . \quad . \quad . \quad (35)$$

Hence the solid is acted on by a wrench (Y, M) whose axis is the axis of y. Thus the axis of the impressed wrench is perpendicular to the central axis of the impulse of the fluid motion, and to the axis of the screw motion of the body.

Let Π be the pitch of the impulse, ϖ the pitch of the screw motion of the solid, P the pitch of the impressed wrench, then

$$\Pi=\frac{\Lambda}{\Xi}, \quad \varpi=\frac{w}{r}, \quad P=\frac{M}{Y},$$

and therefore by (35),

$$P=\varpi+\Pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

is the relation connecting the three pitches.

In particular, if $r=0$ the equations of motion give

$$Z=0, \quad M=w\Xi,$$

showing that a couple M about the axis of y will produce translational motion with velocity M/Ξ along the axis of z.

14. More generally, let the motion be a screw motion about an axis whose inclination to the axis of x is θ and whose shortest distance from that axis is a. Take this shortest distance as the axis of y, and let the screw motion consist of a linear velocity V combined with an angular velocity Ω, the pitch V/Ω being denoted, as before, by ϖ.

It will be readily found that the six components of the screw motion are

$$\left.\begin{array}{ll} u=\mathrm{V}\cos\theta+\Omega a\sin\theta, & p=\Omega\cos\theta, \\ v=0, & q=0, \\ w=\mathrm{V}\sin\theta-\Omega a\cos\theta, & r=\Omega\sin\theta, \end{array}\right\} ; \quad . \quad (37)$$

so that the equations (34) now give

$$\left.\begin{array}{ll} \mathrm{X}=0, & \mathrm{L}=0, \\ \mathrm{Y}=\Omega\Xi\sin\theta, & \mathrm{M}=\mathrm{V}\Xi\sin\theta-\Omega a\Xi\cos\theta+\Omega\Lambda\sin\theta, \\ \mathrm{Z}=0, & \mathrm{N}=0, \end{array}\right\} . (38)$$

The impressed wrench therefore has for its axis the shortest distance between the axis of the screw motion of the solid and the axis of the impulse of the cyclic fluid motion. To find the pitch of the wrench, we have, by division,

$$\frac{\mathrm{M}}{\mathrm{Y}}=\frac{\mathrm{V}}{\Omega}-a\cot\theta+\frac{\Lambda}{\Xi},$$

that is,

$$\mathrm{P}=\varpi-a\cot\theta+\Pi. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

15. In the case of a fine massless circular ring Λ vanishes, or the impulse of the cyclic motion is purely translational. For it is clear that the axis of the ring is the axis of this impulse (the above axis of x), also the fluid motion will evidently be unaffected by rotating the ring about its axis; and therefore the modified function is independent of the angular velocity p.

The equations (34) now become

$$\left.\begin{array}{ll} \mathrm{X}=0, & \mathrm{L}=0, \\ \mathrm{Y}=r\Xi, & \mathrm{M}=w\Xi, \\ \mathrm{Z}=-q\Xi, & \mathrm{N}=-v\Xi. \end{array}\right\} \quad . \quad . \quad . \quad (40)$$

Hence a constant force Y along the axis of y causes uniform rotation with angular velocity Y/Ξ about the axis of z, and a constant couple M about the axis of y causes uniform translational velocity M/Ξ along the axis of z.

It is to be noticed that the impressed wrench never does work in the resulting screw motion, in accordance with the principle of Conservation of Energy.

16. The above results show the effective forces produced by circulation of the fluid on any perforated solid whatever. In the general case the modified function contains the quadratic terms $\mathfrak{T}'+\mathfrak{T}_1$ in addition to the terms of the first degree considered in the above investigation. If we suppose that the solid is moving in any given manner, the six equations of motion (19, 20) determine the components of the impressed wrench (X, Y, Z, L, M, N) necessary to maintain the given

motion. This impressed wrench may be divided into two parts, one being due to the terms $\mathfrak{T}'+\mathfrak{T}_1$ in the modified function, the other being due to the terms

$$\xi u+\eta v+\zeta w+\lambda p+\mu q+\nu r.$$

The first portion is the same as if the motion were acyclic, and represents, therefore, the wrench which would have to be impressed on the solid in order to maintain the given motion if there were no circulation. The second part represents the additional wrench which must be applied on account of the circulations, and the equations to determine it are of the forms found above.

We notice, in particular, that if the solid has any screw motion whose axis coincides with the axis of the impulse of the cyclic fluid motion, the latter wrench vanishes; so that the forces required to maintain the motion are unaffected by the circulations. In other cases the additional wrench is about an axis perpendicular to the axis of the impulse. This is true whatever be the form of the solid and the number of the circulations; but, as has already been pointed out, the position of the axis of the impulse relative to the solid is not in general independent of the circulations unless the solid has but a single aperture.

It is probable that these results might be made to furnish mechanical illustrations of certain physical phenomena; but with these we are not concerned in the present paper.

Note on the foregoing Paper.

Concerning the proper measurement of the impulse of the cyclic motion, a difficulty arises; for, as Mr. Bryan remarks, this motion cannot be set up from rest by impulses applied to the solid alone. Suppose, however, that we close each perforation by a barrier in the usual way, and let the barriers be acted on by the impulsive pressures $\kappa_1\rho$, $\kappa_2\rho$, ... respectively. And instead of these impulsive pressures being due to external forces, *suppose that they are due to some immaterial mechanism attached to the solid.* In general, an impulsive wrench must act on the solid to keep it at rest, and *this wrench is the required impulse of the cyclic motion*; for the only other impulses acting on the system are due to the mutual reactions of the solid and fluid, exerted partly over the surface of the solid and partly through the barriers and attached mechanism, and such mutual reactions cannot affect the impulse. The wrench thus found is of course the same as would be obtained by supposing the impulses on the barriers to be due to *external* impulsive forces, and compounding with these the

impulse *then* necessary to hold the solid at rest. This is in agreement with Prof. Lamb's investigation, which Mr. Bryan has quoted.

More generally, if the solid is in motion, and the liquid is also circulating, we may suppose the instantaneous motion to have been set up from rest by an immaterial mechanism connecting the barriers with the solid at the same time that the requisite external impulses act on the solid. The resultant of these last is, as before, the impulse of the whole motion, and is identical with that found by supposing the barriers actuated by impulses *from without*, and compounding with these the impulse *then* necessary to give to the solid its instantaneous motion.

The same point may be further illustrated by supposing the circulations κ to vary continuously during the motion. To effect this variation we may suppose finite uniform pressures, $P_1 \ldots P_m$, to be exerted over certain ideal surfaces which occupy the positions of barriers. The rate of variation $\dot{\kappa}$ of any circulation is given by $P = \dot{\kappa}\rho$, and in order that it may take place without the direct operation of external forces and couples we may conceive the pressure P to be due, as before, to some highly idealized mechanism attached to the solid. As before, the only forces capable of modifying the impulse are the external forces acting on the solid; and the equations of motion are therefore still to be found by equating the impressed force- and couple-components to the corresponding variations of the "impulse." Since we know the expressions for the impulse-components corresponding to a given instantaneous motion of the solid and given circulations, we have only to remember that in these expressions the κ's are functions of the time, and, just as before, the equations of motion are directly deducible from Hayward's formulæ. Equations (19) (20) of Mr. Bryan's paper will thus be applicable to the present case, provided that in the value of H given by (27) the κ's are allowed to vary.

An investigation proceeding from a consideration of the impulse of the whole motion is not so entirely satisfactory, I think, as the direct method given by Mr. Bryan; but, at the same time, this brief attempt to interpret the impulse of the cyclic motion may not be without interest.—C. V. Burton.

Note added by the Author.

Dr. Burton's note is of much value as showing more exactly what is meant by the "impulse" of the motion in the

ordinary investigations given by Prof. Lamb, and, in a less intelligible form, by Basset.

The equations of motion under finite forces may be deduced by equating the change of momentum in a small time-interval δt to the impulse of the impressed forces, taking into account the fact that in the interval δt the origin has a displacement of translation $(u\delta t, v\delta t, w\delta t)$ and the axes have rotational displacements $(p\delta t, q\delta t, r\delta t)$, so that the final momenta are referred to a different set of axes to the original momenta.

The mode of forming the equations of motion is given by Prof. Greenhill (*Encyclopædia Britannica*, art. "Hydromechanics") for the case of acyclic motion, but it is hardly so obvious *why* in thus forming the equations of motion of a perforated solid, it is necessary to include in the "impulse" terms representing the components of the wrench applied to the *barriers* as well as to the solid. We may, however, suppose the changes which actually occur in the time δt to have been produced as follows :—

1st. Let the solid and fluid be reduced to rest by an impulsive wrench applied to the solid, and transmitted to a series of barriers crossing the perforations. The components of this wrench will be found to be

$$\frac{\partial T}{\partial u} + \xi, \text{ \&c.}, \ldots \frac{\partial T}{\partial p} + \lambda, \text{ \&c.} \ldots$$

2nd. The barriers being rigidly connected with the solid, let the latter receive small displacements whose translational and rotational components are $(u\delta t, v\delta t, w\delta t, p\delta t, q\delta t, r\delta t)$ and let the solid come to rest in its new position. The fluid will evidently also come to rest, and therefore no impulse will be impressed on the system by this change (as may be otherwise seen by supposing the change to take place very slowly).

3rd. Let the solid be set in motion with velocity-components $(u + \partial u/\partial t \,.\, \delta t, \ldots, p + \partial p/\partial t \,.\, \delta t \ldots)$ referred to the new positions of the axes, and let the circulations κ be started in the new position of the solid by a suitable impulsive wrench applied to the solid and transmitted from it to the barriers.

Then the impulse of the impressed forces (components $X\delta t \ldots$, $L\delta t \ldots$) is the resultant of the wrenches required to stop the whole system in the first process and to start it again in the third.

It is, therefore, that impulse which must be compounded with the total impulse in the initial position in order to obtain the total impulse in the final position.

Whence Hayward's equations of motion follow at once (as

shown in Greenhill's article above referred to), and they take the form of the above equations (14), (15).

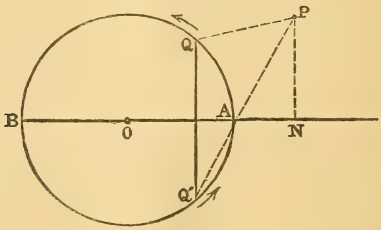
If we were merely to stop the solid in the first process without stopping the liquid, the cyclic motion would cause the liquid to exert a pressure on the solid in the second process, and the impulse of this pressure would not be zero, but would have to be taken into account in forming the equations of motion. It would be wrong, therefore, to deduce the equations of motion from the impulse applied to the solid alone, as is evident in the analogous case of a solid containing one or more gyrostats.

XXXV. *The Magnetic Field of a Circular Current.* *By* Professor G. M. Minchin, *M.A.**

CLERK MAXWELL gives a method of drawing the lines of magnetic force due to a circular current ('Electricity and Magnetism,' Art. 702) by means of a series of circles and a series of parallel lines. The object of the following paper is to show how these curves can be described by a slightly different method, and to exhibit the geometrical connexion of the series of circles.

Let AQBQ′ be the circular current whose sense is indicated by the arrows, the plane of the circle being that of the paper;

Fig. 1.



let P be any point in space, PN the perpendicular from P on the plane of the circle, and NAOB the diameter of the circle drawn through N. We shall calculate the *vector potential* of the current at P.

Draw any ordinate, QQ′, of the circle perpendicular to BA; and consider two equal elements of length of the circle, each equal to ds, at Q and Q′. Resolving each of these along and perpendicular to QQ′, we see that the latter components are in opposite senses, and hence their vector potentials at P cancel

* Communicated by the Physical Society: read March 10, 1893.

each other, since PQ = PQ′. If ψ is the angle QOA, a = radius of circle, i = current strength, the components of ids along Q′Q being equal and in the same sense, the two elements of current at Q′ and Q conspire in giving a vector potential $\frac{2i\cos\psi}{\text{PQ}}.ds$ perpendicular to the plane PON. Hence the total vector potential at P is perpendicular to the plane PON. If, therefore, OA is the axis of x, the perpendicular at O to the plane of the circle the axis of z, and the diameter at O perpendicular to AB the axis of y, the components of the vector potential being, as usual, denoted by F, G, H, the only component existing is G; but, by taking the components of the vector potential at a point indefinitely close to P in the direction of the axis of y, we easily find that

$$\frac{d\text{F}}{dy} = -\frac{\text{G}}{\alpha}.$$

Hence if X, Y, Z are the components of the force of the current per unit magnetic pole at P, since this force is the curl of the vector potential, we have

$$\text{X} = -\frac{d\text{G}}{d\gamma}, \quad \text{Y} = 0, \quad \text{Z} = \frac{d\text{G}}{d\alpha} + \frac{\text{G}}{\alpha},$$

where α (=ON) and γ (=NP) are the coordinates of P. If along the line of force at P the increments of the coordinates are $\Delta\alpha$, $\Delta\gamma$, we have

$$\frac{\Delta\alpha}{\Delta\gamma} = \frac{\text{X}}{\text{Z}}.$$

Hence along this line we have

$$\frac{d\text{G}}{d\alpha}\Delta\alpha + \frac{d\text{G}}{d\gamma}\Delta\gamma + \frac{\text{G}}{\alpha}\Delta\alpha = 0,$$

i.e., $\text{G}.\alpha$ = constant along the line of force.

We shall therefore calculate the vector potential, G, at P.

Evidently

$$\text{G} = 2i\int_0^\pi \frac{\cos\psi}{\text{PQ}}.ds$$

$$= 2ia\int_0^\pi \frac{\cos\psi\,.\,d\psi}{\sqrt{\alpha^2+a^2+\gamma^2-2a\alpha\cos\psi}}$$

$$= \frac{i}{\alpha}\int_0^\pi \frac{\alpha^2+a^2+\gamma^2}{\text{D}} - \text{D}\Big)\,d\psi,$$

denoting the denominator by D. Now let $\psi=\pi-\omega$, and let $\rho^2=(\alpha+a)^2+\gamma^2$, $\rho'^2=(\alpha-a)^2+\gamma^2$, so that $\rho=\mathrm{PB}$, $\rho'=\mathrm{PA}$. Then

$$\mathrm{G}=\frac{i}{2\alpha}\int_0^\pi\left\{\frac{\rho^2+\rho'^2}{\rho}\cdot\frac{1}{\Delta}-2\rho\Delta\right\}d\omega,$$

where

$$\Delta=\sqrt{1-\left(1-\frac{\rho'^2}{\rho^2}\right)\sin^2\frac{\omega}{2}}.$$

Let $\omega=2\phi$, and $k^2=1-\frac{\rho'^2}{\rho^2}$; then, finally,

$$\mathrm{G}=\frac{4ia}{\rho}\left\{\frac{2}{k^2}(\mathrm{K}-\mathrm{E})-\mathrm{K}\right\},$$

where K and E are the complete elliptic integrals of the first and second kinds with modulus k; so that the quantity in brackets is a function of the ratio $\frac{\mathrm{PA}}{\mathrm{PB}}$ simply.

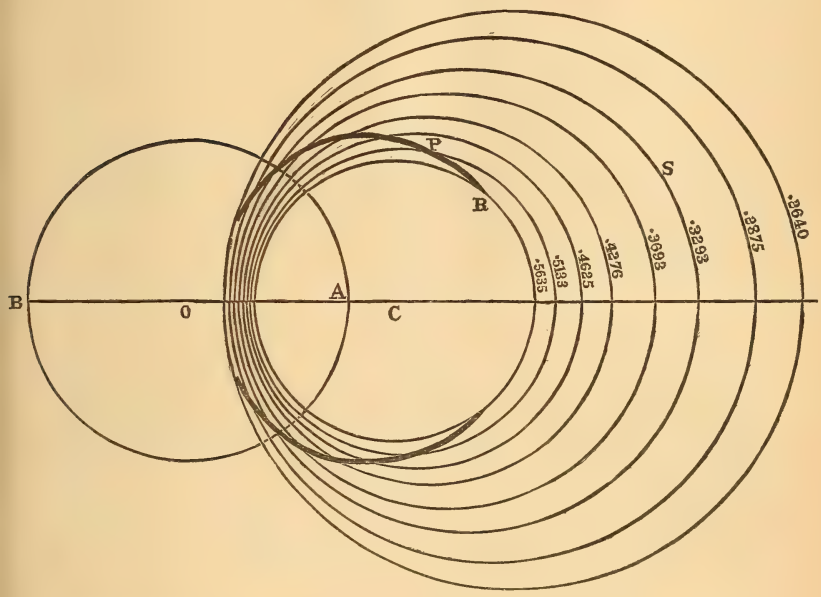
Also, since $\rho^2-\rho'^2=4a\alpha$, we have $\alpha=\frac{\rho^2k^2}{4a}$, and the quantity $\mathrm{G}\,.\,\alpha$ which is constant along the line of force is given by the equation

$$\mathrm{G}\,.\,\alpha=i\rho\{2(\mathrm{K}-\mathrm{E})-k^2\mathrm{K}\}.$$

It is thus seen that at every point in space G is of the form $\frac{1}{\rho}f\left(\frac{\rho'}{\rho}\right)$; so that at all points on the surface for which $\frac{\rho'}{\rho}$ is a constant, the value of G will vary inversely as ρ. The surface for which $\frac{\rho'}{\rho}$ is constant is a sphere having its centre on the line BA produced and cutting the sphere having BA for diameter orthogonally. If we assign a series of values to the ratio $\frac{\rho'}{\rho}$, we obtain a series of spheres having their centres on BA and cutting the given sphere orthogonally, the radius of each sphere of the series being, therefore, the length of a tangent from its centre to the sphere described on BA; for, given the base, BA, of a triangle, and the ratio of the sides, the locus of the vertex is a circle whose diameter is the join of the points which divide BA internally and externally in the given ratio. The surface locus of the vertex is the sphere generated by the revolution of this circle.

On account of the symmetry of the current round its axis through O, the lines of force and those of constant vector potential are the same in all planes through the axis. We may, then, confine our attention to the plane PON, and suppose fig. 2 to be in this plane, the current being

Fig. 2.



in this figure represented in projection by the line BA. Describe a series of circles having their centres on BA produced and cutting the circle described on BA as diameter orthogonally. Along each of these circles, then, the ratio $\frac{PA}{PB}$ is constant, P being any point on the circle.

Consider first the lines of constant vector potential. For each of the circles let the value of the quantity $\frac{2}{k^2}(K-E)-K$ be calculated. Denote this quantity by Q for any one circle; then

$$G = \frac{4Qia}{\rho};$$

so that if we wish to trace out the line of constant vector potential for which G has any given value, we can find the point, P, in which it cuts any circle of the series by measuring

the length PB such that

$$\mathrm{PB} = \frac{4\mathrm{Q}i}{\mathrm{G}} \cdot a.$$

Let PT be any circle of the co-orthogonal series cutting BA at n and m. Then for this circle

$$\frac{\rho'}{\rho} = \frac{\mathrm{A}n}{\mathrm{B}n} = \frac{m\mathrm{A}}{m\mathrm{B}};$$

and if this ratio is denoted by s, it is well known that

$$\frac{\mathrm{CA}}{\mathrm{CB}} = s^2,$$

where C is the centre of the circle. Now the modulus, k, of the elliptic integrals which belongs to the circle $m\mathrm{P}n$ is $\left(1-\frac{\mathrm{PA}^2}{\mathrm{PB}^2}\right)^{\frac{1}{2}}$, *i.e.* $k^2=1-s^2$; hence

$$k^2 = \frac{\mathrm{AB}}{\mathrm{BC}},$$

or the square of the modulus is inversely proportional to the distance, BC, of the centre of the circle from B.

The circles employed by Clerk Maxwell in drawing the lines of force can be easily shown to be this co-orthogonal system whose centres are ranged along BA produced. For, his rule is to assign a series of values to θ, and construct a series of circles whose centres lie on BA, the radius of each being $\frac{a}{2}(\operatorname{cosec}\theta - \sin\theta)$, while the distance of its centre from O is $\frac{a}{2}(\operatorname{cosec}\theta + \sin\theta)$; the modulus belonging to this circle is $\sin\theta$. For the series of circles he then calculates the values of the expression (constant for each circle) $\frac{\sin\theta}{(\mathrm{K}-\mathrm{E})^2}$, and the point on each circle which lies on any assigned line of force is found by drawing a certain right line perpendicular to BA. It is at once found that this series of circles is precisely the co-orthogonal system above described; but Clerk Maxwell's modulus is not the same function of the ratio $\frac{\rho'}{\rho}$, or of the radius of the circle selected, as that adopted above; for, with Clerk Maxwell, if r is the radius of any circle of the series and k the corresponding modulus,

$$r = \frac{a}{2}\left(\frac{1}{k} - k\right),$$

whereas above we have

$$r = \frac{2\sqrt{1-k^2}}{k^2} \cdot a.$$

Of course (as stated in a note by Clerk Maxwell) the elliptic integrals depending on the one modulus can be transformed into elliptic integrals depending on the other; and in this case the transformation is the well-known one of Lagrange. But the constructions for the points in which any given line of force cuts the series of circles will not be the same in both cases—those of Clerk Maxwell depending on a series of right lines perpendicular to BA, and those above indicated depending on a series of radial distances from B.

When we propose to draw the line of constant vector potential through any point, P, which lies on a circle whose constant is Q_0, let PB be ρ_0; then the point, R, in which this line meets any other circle, whose constant is Q, is found from the relation

$$\rho = \rho_0 \frac{Q}{Q_0},$$

where $\rho = BR$.

This latter method has a certain advantage for the eye, inasmuch as it enables us to see readily those circles of the series outside which the line of constant vector potential through any proposed point lies.

Consider now the lines of force. With the above value of Q, the quantity which is constant along a line of force is $\rho . k^2 Q$, so that on each of the above circles in fig. 2 we must now mark the number $k^2 Q$. Denote this by Q'. Then the above relation for points on the same line of constant vector potential becomes for the lines of force

$$\rho = \rho_0 \frac{Q_0'}{Q'},$$

and the construction proceeds in the same way. The constants, Q', for the above series of circles, beginning at the innermost, are :—

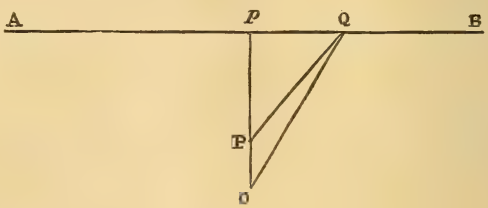
·4841 ; ·4301 ; ·3775 ; ·3396 ; ·2782 ; ·2376 ; ·1954 ; ·1727.

The values of the Q's diminish outwards for the circles; so that if we consider the line of vector potential at any point, S, suppose, which is such that SB is greater than the distance from B of the point along AC in which any circle interior to that passing through S cuts the line BAC, it is at once obvious that the line of vector potential which belongs to S is wholly outside all such circles. The numerical values of Q for the

circles in fig. 2 are marked at the circumferences, and as much of the line of potential belonging to P is drawn as is justified by the number of circles represented in the figure.

The fundamental proposition of electromagnetism is that the intensity of magnetic force produced at any point in presence of electric currents is the curl of the vector potential

Fig. 3.



at the point. But if in the field there is a current in an infinitely long straight wire, AB, we find that at every point in the field the vector potential due to this current is infinite. Hence it seems impossible to deduce the magnetic force, and the lines of magnetic force, from the above fundamental proposition. This result is unsatisfactory, and it manifestly points to some defect in our definition of the vector potential.

We are presented with a similar unsatisfactory result in the general theory of gravitation potential. Thus, taking the common definition of gravitation potential, if AB is a limited uniform bar attracting according to the law of inverse square, we know that the potential which it produces at any point, P, is proportional to $\log\left(\cot\frac{A}{2}\cot\frac{B}{2}\right)$, where $A=\angle PAB$, $B=\angle PBA$. Now, if the rod extends to infinity, this expression becomes infinite. I have shown ('Statics,' vol. ii. Art. 332) how this difficulty arises, and how it is to be remedied by mending the definition of potential. The difficulty is avoided in a similar manner with regard to the vector potential.

Thus, since we are concerned only with differential coefficients of the vector potential, the ordinary components, F, G, H of this vector may have added to them any *constant* quantities whatever. This amounts to saying that the vector potential at any variable point, P, in the field is the vector potential at any *fixed* point, O, plus the vector difference between P and O. It does not matter whether the vector at O is infinite or not: it is a constant in the field. As in the general gravitation field we are concerned with *differences*

of potential only, so in the electromagnetic field we are concerned with vector differences only.

Let us, then, calculate for the infinite straight current AB the vector difference between P and a point O on the perpendicular, Pp, at a constant distance O$p=a$ from the line.

Let P$p=r$, and let an element, ds, of the line AB be taken at any point, Q; let $\angle p\mathrm{PQ}=\theta$. Then the vector difference, due to this element, at P is $\frac{ds}{\mathrm{QP}}-\frac{ds}{\mathrm{QO}}$, or

$$\left\{1-\frac{r}{\sqrt{r^2+(a^2-r^2)\cos^2\theta}}\right\}\cdot\frac{d\theta}{\cos\theta}.$$

Double the integral of this from $\theta=0$ to $\theta=\frac{\pi}{2}$ is the vector difference at P due to unit current in AB. Expanding the radical in ascending powers of $\lambda\left(\equiv\frac{a^2-r^2}{r^2}\right)$, we have the vector equal to

$$2\int_0^{\frac{\pi}{2}}\left\{\tfrac{1}{2}\lambda-\frac{1.3}{2.4}\lambda^2\cos^2\theta+\frac{1.3.5}{2.4.6}\lambda^3\cos^4\theta-\ldots\right\}d(\sin\theta)$$
$$=\lambda-\tfrac{1}{2}\lambda^2+\tfrac{1}{3}\lambda^3-\tfrac{1}{4}\lambda^4+\ldots$$

and this $=\log_e(1+\lambda)=2\log\frac{a}{r}$. Thus, then, the vector difference at any point, P, is measured by

$$\mathrm{C}-2\log r,$$

where C is a constant; and this gives the known value of the magnetic force at P, viz., $-\frac{d\mathrm{G}}{dr}$ (where G is the vector potential), perpendicular to the plane PAB, *i.e.* $\frac{k}{r}$, where k is a constant. In this way, then, the inconvenience of dealing with an infinite vector potential in presence of an infinitely long (or very long) straight current is avoided.

The lines of constant magnetic potential, or the loci of points, P, at which the given circular current subtends a constant conical ("solid") angle, are the orthogonal trajectories of the lines of force, and can be drawn when these lines are drawn.

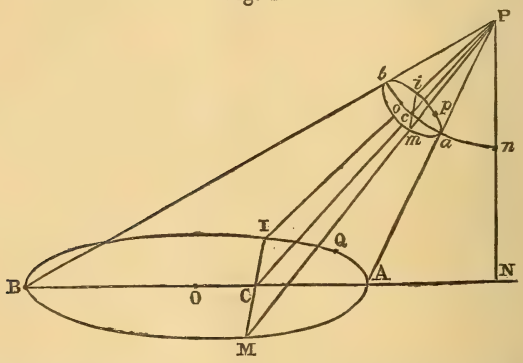
It is not easy to draw these equipotential curves independently, or even to deduce their typical equation from that of

the lines of force by the mathematics of orthogonal trajectories.

The magnitude of the conical angle subtended at any point by a given circle can be expressed in finite terms by means of complete elliptic integrals of the third kind. The parameter involved in these integrals will depend on the way in which they are taken.

If a sphere of unit radius is described round P as centre, and lines are drawn from P to the points on the circumference of the given circle, BMAI, fig. 4, these lines will intercept on the sphere a spherical ellipse, *bmai*, whose area is the conical angle subtended by the circle at P. The minor axis of this ellipse is the great circular arc *ab* determined by the lines PA, PB, while the major axis, *mi*, is determined by the chord, MI, of the circle which subtends a maximum angle, MPI, at P. This line is determined by drawing the bisector,

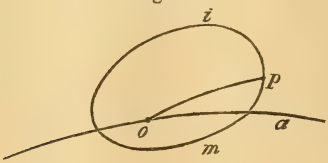
Fig. 4.



PC, of the angle BPA, meeting BA in C; then MI is the chord through C perpendicular to the plane BAP. The point *c* in which PC meets the surface of the sphere is the centre of the spherical ellipse.

Now, given any curve, *mpi*, fig. 5, on a sphere of unit

Fig. 5.



radius, its area is $\int(1-\cos\theta)d\phi$, where, if o is any point on the sphere *inside* the area, θ is the circular measure of the

spherical radius vector op drawn to any point, p, of the curve, and ϕ is the angle between the radius op and any fixed arc, oa, drawn at o. If, as said, the pole o is inside the area, ϕ goes from o to 2π; but if o is *outside* the curve, the area has a different expression, viz.:—

$$\int_0^o \cos\theta d\phi,$$

the longitude angle ϕ obviously starting and ending with a zero value. If o is *on* the curve, the expression for the area is again different.

In calculating the area of the above ellipse it would be natural to choose for pole (o) the point n in which the sphere is cut by the line PN; but this leads to difficulties when the position of P is such that n falls on the ellipse. This will happen when P is on any perpendicular to the plane of the circle of the current drawn at any point on its circumference; and, moreover, the choosing of n for pole will lead to expressions for the conical angle which present its values in forms which are apparently discontinuous for points P which project inside and outside the area of the given circle BMA1. Such discontinuity must not exist, and to get rid of it from the expressions requires troublesome transformations of elliptic integrals of the third kind.

We must, then, choose for pole a point which is always inside the spherical ellipse. The simplest point is the point o (fig. 4), in which the sphere is cut by the line PO which joins P to the centre, O, of the given circle. This point is, of course, always inside the ellipse.

Let, then, Q be any point on the given circuit, and p the point in which PQ cuts the ellipse. Taking for the fixed plane of longitude through o the plane baP, or BAP, and denoting the angle poa by ϕ, the area of the ellipse is

$$\int_0^{2\pi}(1-\cos op)d\phi, \text{ i. e., } 2\pi-\int_0^{2\pi}\cos op\,.\,d\phi.$$

Denoting, as before, the position of Q by the angle ψ, or QOA, we easily find, if PN$=z$, PO$=r$, ON$=x$,

$$d\phi=\frac{rz}{z^2+x^2\sin^2\psi}\,.\,d\psi,$$

$$\cos op=\frac{r^2-ax\cos\psi}{r\sqrt{r^2+a^2-2ax\cos\psi}},$$

Hence

$$\int_0^{2\pi}\cos op\,.\,d\phi=2z\int_0^{\pi}\frac{r^2-ax\cos\psi}{\sqrt{r^2+a^2-2ax\cos\psi}}\cdot\frac{d\psi}{z^2+x^2\sin^2\psi}.$$

Putting $\psi=\pi-\chi$, this becomes

$$2z\int_0^\pi \left\{\rho\sqrt{1-k^2\sin^2\frac{\chi}{2}}+\frac{r^2-a^2}{\rho\sqrt{1-k^2\sin^2\frac{\chi}{2}}}\right\}\frac{d\chi}{z^2+x^2\sin^2\chi},$$

where, as before, $\rho=\mathrm{PB}$, $\rho'=\mathrm{PA}$, and $k^2=1-\frac{\rho'^2}{\rho^2}$. If we put $\chi=2\omega$, this becomes

$$z\int_0^{\frac{\pi}{2}}\left(\rho\Delta+\frac{r^2-a^2}{\rho\Delta}\right)\frac{d\omega}{z^2+x^2\sin^2 2\omega},$$

where $\Delta\equiv\sqrt{1-k^2\sin^2\omega}$.

To reduce this to elliptic integrals, we must resolve the fraction $1/z^2+x^2\sin^2 2\omega$ into two fractions. It is easily found that

$$z^2+x^2\sin^2 2\omega=z^2+4x^2(\sin^2\omega-\sin^4\omega)$$
$$=(\sqrt{z^2+x^2}+x-2x\sin^2\omega)(\sqrt{z^2+x^2}-x+2x\sin^2\omega).$$

Let ν denote the sine of the angle between PO and the axis of the current (or PN); then the expression, after resolution into partial fractions, becomes

$$\frac{z}{2r^2}\int_0^{\frac{\pi}{2}}\left(\rho\Delta+\frac{r^2-a^2}{\rho\Delta}\right)\left(\frac{1}{1-\nu+2\nu\sin^2\omega}+\frac{1}{1+\nu-2\nu\sin^2\omega}\right)d\omega.$$

The portion of this expression which has Δ in the denominator is at once the sum of two complete elliptic integrals of the third kind; and the portion which has Δ in the numerator is easily reduced to the same form. The result is

$$\frac{z}{r\rho}\int_0^{\frac{\pi}{2}}\left(\frac{r+a}{\mathrm{N}\Delta}+\frac{r-a}{\mathrm{N}'\Delta}\right)d\omega,$$

where $\mathrm{N}\equiv 1-\nu+2\nu\sin^2\omega$, and N' is the value of N when ν is changed to $-\nu$. Hence we have two elliptic integrals of the third kind, one with $\left(\frac{2\nu}{1-\nu},\ k\right)$ for parameter and modulus, and the other with $\left(\frac{-2\nu}{1+\nu},\ k\right)$. In the usual notation, then, we have for the complete expression of the conical angle subtended by the circuit at P the value

$$2\pi-\frac{2z}{\rho r}\left\{\frac{r+a}{1-\nu}\Pi\left(\frac{2\nu}{1-\nu},\ k\right)+\frac{r-a}{1+\nu}\Pi\left(\frac{-2\nu}{1+\nu},\ k\right)\right\}.$$

Of course it is not pretended that this expression is the most convenient for the purposes of calculation: the approximate value of the conical angle which is given by a series of spherical harmonics is that which should be employed; but it may be well to give the *complete* expression in the above form, which I have not seen published anywhere.

XXXVI. *On Hydrolysis in Aqueous Salt-Solutions.* *By* John Shields, *B.Sc., Ph.D.**

On dissolving potassium cyanide in water it is partially decomposed into potassium hydrate and hydrogen cyanide. This action of the water in producing decomposition is called hydrolysis. Probably all salts are hydrolysed in aqueous solution to a certain extent, but in the majority of cases the amount of hydrolysis is so excessively small that the means which we have at our command are not sufficiently delicate to enable us to detect it. Besides the salts there is another important class of compounds, namely the esters, which are susceptible to hydrolysis on being mixed with water. Methyl and ethyl acetate, for example, are decomposed by water to a considerable extent into acetic acid and the corresponding alcohol. The extent to which hydrolysis takes place is regulated by the law of mass action as enunciated by Guldberg and Waage. In all cases we are dealing with a state of chemical equilibrium or balanced action which is usually represented thus :—

$$KCN + HOH \rightleftharpoons KOH + HCN,$$

or

$$CH_3COOC_2H_5 + HOH \rightleftharpoons C_2H_5OH + CH_3COOH,$$

the sign $\rightleftharpoons$ being substituted for the ordinary sign of equality as suggested by Van't Hoff.

Now, *à priori*, we should expect a substance, for example potassium cyanide, which is formed from chemically equivalent quantities of acid and base to be neutral, and we have every reason to believe potassium cyanide, as such, to be so. Its solution in water, however, as is well known, has a strongly alkaline reaction, and the above explanation of hydrolysis furnishes us with no reason why the solution should react alkaline rather than acid, since the hydrolysed fraction of the potassium cyanide still exists in the solution as chemically equivalent quantities of acid and base. Here Arrhenius' theory of electrolytic dissociation comes to our aid, and shows us that although we may have in the solution equivalent

* Read before the Swedish Academy of Science, Stockholm, 11th January, 1893. Communicated by the Author.

quantities of potassium hydrate and hydrogen cyanide, yet the former is very largely dissociated into its ions, and, therefore, in a particularly favourable state for entering into reaction with the indicator, whilst the latter is not so. According to the same theory, if we add other salts to a solution of hydrocyanic acid, which, *per se*, is only slightly electrolytically dissociated, then the amount of dissociation is diminished many thousand times, and this is practically what occurs in the solution under consideration. The presence of the unhydrolysed potassium cyanide causes the dissociation ratio of the hydrocyanic acid to be vastly decreased.

There are salts, on the other hand, whose solutions have an acid reaction. This is due to the fact that the acid, which is one of the products of hydrolysis, is more highly electrolytically dissociated than the base which is formed at the same time. Usually the above facts are expressed by saying that the base is stronger than the acid, or *vice versâ*.

If hydrocyanic acid were as nearly completely dissociated as hydrochloric acid is, at the same dilution of course, then probably a solution of potassium cyanide would be as nearly neutral as one of potassium chloride, for Ostwald has pointed out that all acids when completely dissociated are equally strong.

In this memoir, salts of strong bases with weak acids only have been considered. The investigation was undertaken at the suggestion of Dr. Svante Arrhenius, in Stockholm, and the main object in view was the determination of the amount of free alkali in aqueous solutions of such salts as potassium cyanide, sodium carbonate, &c.; that is, of salts whose solutions exhibit an alkaline reaction, or act as mild alkalies.

I should like to avail myself of this opportunity to express to Dr. Arrhenius my warmest thanks for the help which he so willingly gave me and for the interest which he all along took in the work.

A research, "Zur Affinitätsbestimmung organischer Basen" (*Zeits. f. physikal. Chemie*, vol. iv. p. 319, 1889), on somewhat similar lines, has already been carried out by Dr. James Walker. In it the relative strengths of different organic bases were measured; but one of the experimental methods which he adopted could have served equally well for the determination of the amount of free acid in aqueous solutions of salts of the bases.

As a general rule, it will be found that the determination of the amount of free alkali in solutions of the above salts is beyond the scope of ordinary analysis. A reaction which enables us to do so, however, is known. The velocity with which the salt-solutions saponify methyl or ethyl acetate gives

us a measure of the quantity of free alkali which they contain. The essential condition for saponification to take place is the presence of hydrogen or hydroxyl ions. Now Walker's method was based on the presence of hydrogen ions, whilst in the experiments about to be described we are dealing with hydroxyl ions. This places us, as it were, on vantage ground; for, since hydroxyl ions saponify much more rapidly than hydrogen ions, it is thus possible to work with more dilute solutions where perturbing influences are reduced to a minimum.

To return once more to the typical example of the salts under investigation, potassium cyanide, let us for a moment consider what takes place when we dissolve this body in water. Besides the undissociated KCN we get a great number of $\overset{+}{K}$ and $\overset{-}{CN}$ ions, the water itself, too, is slightly dissociated into $\overset{+}{H}$ and $\overset{-}{OH}$ ions. Now the $\overset{+}{H}$ ions coming into contact with the $\overset{-}{CN}$ ions unite with them to form HCN which is uncharged, being practically undissociated, whilst the hydroxyl ions remain free and counterbalance the potassium ions.

The water goes on continually supplying hydrogen and hydroxyl ions, which are disposed of in this way, until equilibrium takes place. If we now make up a small inventory of the *principal* constituents of the solution we get:—

1 and 2, $\overset{+}{K}$ and $\overset{-}{CN}$ ions.
3, KCN undissociated.
4, HOH undissociated (say).
5, HCN undissociated (say), and, corresponding to this,
6 and 7, $\overset{+}{K}$ and $\overset{-}{OH}$ ions.

6 and 7 taken together represent the quantity of free potash present in the solution. The task which now lies before us is comparatively easy, but before proceeding to deduce formulæ for the calculations it is as well to point out what will be proved later on, namely, that potassium cyanide itself is not an active agent of saponification. Attention may also be directed to the fact that the dissociation of the hydrogen cyanide is so excessively slight in presence of the salt, that it cannot exercise any appreciable influence on the velocity of saponification: the truth of this will be the more readily admitted if we bear in mind that hydrogen ions are much less active than hydroxyl ions. What has already been said regarding the influence of the salt on the dissociation of the hydrogen cyanide applies equally well to the water.

When ethyl acetate is saponified by a solution of potassium

hydrate, the velocity of the reaction is represented at every instant by the general equation

$$\frac{dx}{dt} = k(C-x)(C_1-x), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the coefficient of velocity of reaction, C and C_1 the concentrations of the ester and base respectively at the commencement, and x the quantity of ester which has undergone change during the time t.

In the case of the salt-solutions we wish to determine the concentration of the base, *i.e.*, the amount of active free alkali at the commencement, the coefficient of velocity for the various bases being already known. On dissolving potassium cyanide in water we get

$$KOH + HCN \rightleftharpoons KCN + HOH$$

(quantity KOH × diss. ratio) × (quantity HCN × diss. ratio)
= (quantity KCN × diss. ratio) × (quantity HOH × diss. ratio).

The dissociation ratios of potassium cyanide and potassium hydrate, water and hydrogen cyanide, do not alter appreciably with change of concentration in the solution, and may consequently be regarded as constant. (Arrhenius, *Zeits. f. physikal. Chemie*, vol. v. p. 17, 1890.)

The quantity of water as compared with the other substances is supposed to be infinitely great and regarded as a constant K. The saponification of ethyl acetate by means of aqueous potash takes place according to the equation :—

$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH\ ;$$

and if we represent by C_2 the initial concentration of the potassium cyanide, by A the concentration of the free potassium hydrate, and by x that of the potassium acetate formed, then $C_2 - x - A$ will represent the actual concentration of the potassium cyanide, and $A + x$ that of the hydrocyanic acid ; all of course being expressed in the same unit, namely, gram-molecules per litre. From the equilibrium,

$$KOH + HCN \rightleftharpoons KCN + HOH$$

we now get, using our new symbols, the equation

$$A(A+x) = K(C_2 - x - A), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which represents what takes place at any stage of the reaction. After the first few moments, however, when A becomes very small compared with x, we may write the equation thus :—

$$A = \frac{K(C_2 - x)}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3$$

Now, in the general equation (1) C_1-x the concentration of the base is what we now call A, so that we may re-write it in the form

$$A=\frac{dx}{dt}\cdot\frac{1}{C-x}\cdot\frac{1}{k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Combining (3) and (4) we get

$$\frac{dx}{dt}\cdot\frac{1}{C-x}\cdot\frac{1}{k}=\frac{K(C_2-x)}{x}, \quad . \quad . \quad . \quad . \quad (5)$$

which on integration gives the solution :

$$K=\frac{\frac{C_2}{C-C_2}\log\text{nat.}\frac{C_2-x_0}{C_2-x_1}-\frac{C}{C-C_2}\log\text{nat.}\frac{C-x_0}{C-x_1}}{k(t_1-t_0)}. \quad (6)$$

k, the specific coefficient of velocity, is known, and for potash at 24°·2 C. is numerically equal to 6·22. Having got K from equation (6) all that remains to be done in order to know how much free potash is present in the solution at the commencement is the calculation of A from equation (2). At the beginning, when $x=0$,

$$A^2=K(C_2-A), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from which we get A in gram-molecules per litre.

The percentage amount of potassium cyanide which has been decomposed by the water is therefore

$$\frac{100\,A}{C_2}.$$

It is here unnecessary to describe in detail the apparatus and method which I used to determine the velocity of the saponification of ethyl acetate by the salt-solutions, as it was precisely similar to that which has already been employed by Ostwald (*Journ. f. pr. Ch.* [2] vol. xxxv. p. 112, 1887), Arrhenius (*Zeits. f. physikal. Chemie*, vol. i. p. 110, 1887), and others. Measured volumes of a known strength of salt-solution and of ethyl acetate were mixed at the temperature of the thermostat. (For the construction of the thermostat, &c. see *Zeits. f. physikal. Chemie*, vol. ii. p. 564, 1888.) From time to time small fractions of the mixture were withdrawn by means of a pipette and titrated as expeditiously as possible.

In calculating the concentration of the salt at the commencement, it has been assumed that the volume of the mixed solutions of salt and ester is the sum of the volumes taken separately. This is of course, strictly speaking, not true, but the deviation from the truth is so small as to be entirely negligible. I shall now proceed to give the experimental

results which I obtained. The first column in the tables contains the time t expressed in minutes since the beginning of the reaction. The second and fourth columns C_2-x and $C-x$ contain the concentrations of the salt and ester respectively in hundredths of a gram-molecule per litre. The third column contains x the quantity of ester which has undergone change, also expressed in the same unit. In the last column will be found the constant expressed in arbitrary units. Here it may be noticed that the first few values have been neglected in accordance with the derivation of the formula. From the mean value of these the characteristic constant K has been calculated. A represents the amount of free alkali in gram-molecules per litre, and besides this will be found the percentage amount of salt which has been hydrolysed in the solution experimented on and at the temperature at which the experiment was carried out. It is conceivable that the addition of ethyl acetate to the solution of salt would disturb the existing equilibrium, but a discussion of this question is reserved for a later part of the memoir.

Potassium Cyanide.

Solutions of this salt of four different concentrations were examined, namely, $\frac{1}{1}$, $\frac{1}{4}$, $\frac{1}{10}$, and $\frac{1}{40}$ normal. The temperature at which the experiments were made was 24°·2 C. The value of k, the coefficient of velocity for potash at this temperature, is 6·22. Nitrophenol was found to be the most suitable indicator, and enabled me when titrating with decinormal hydrochloric acid to observe the end point pretty accurately.

$\frac{N}{1}$ Potassium Cyanide.

t.	C_2-x.	x.	$C-x$.	
0	94·74	0·00	39·34	
4	93·40	1·34	38·00	
16	92·28	2·46	36·88	$(313)\times10^{-7}$
30	91·40	3·34	36·00	324
90	88·72	6·02	33·32	385
210	86·40	8·34	31·00	337
353	84·20	10·54	28·80	342
580	81·20	13·54	25·80	378
				Mean $=353\times10^{-7}$

K = 0·000928.
A = 0·00296, or 0·31 per cent. of salt hydrolysed.

$\frac{N}{4}$ Potassium Cyanide.

t.	C_2-x.	x.	$C-x$.	
0	23·48	0·00	39·34	
6	22·52	0·96	38·38	
19	21·98	1·50	37·84	$(117)\times10^{-7}$
34	21·50	1·98	37·36	189
95	20·12	3·36	35·98	219
213	18·68	4·80	34·54	216
347	17·44	6·04	33·30	226
584	15·98	7·50	31·84	226
1394	13·00	10·48	28·86	225
2789	9·82	13·66	25·68	245
				Mean $=221\times10^{-7}$

K = 0·00121.

A = 0·00168, or 0·72 per cent. of salt hydrolysed.

$\frac{N}{10}$ Potassium Cyanide.

t.	C_2-x.	x.	$C-x$.	
0	9·52	0·00	48·70	
2	9·23	0·29	48·41	
6	8·87	0·65	48·05	$(251·5)\times10^{-6}$
12·5	8·67	0·85	47·85	123·8
33	8·15	1·37	47·33	126·1
60	7·67	1·85	46·85	131·2
130	6·78	2·74	45·96	145·1
209	6·25	3·27	45·43	133·7
319	5·56	3·96	44·74	141·8
1372	2·93	6·59	42·11	137·6
				Mean $=133·8\times10^{-6}$

K = 0·001204.

A = 0·00107, or 1·12 per cent. of salt hydrolysed.

$\frac{N}{40}$ Potassium Cyanide.

t.	C_2-x.	x.	$C-x$.	
0	2·38	0·00	48·70	
2	2·20	0·18	48·52	
4·5	2·10	0·28	48·42	$(449)\times10^{-6}$
8·5	2·00	0·38	48·32	732
22	1·83	0·55	48·15	602
44	1·59	0·79	47·91	683
112	1·17	1·21	47·49	759
191	1·00	1·38	47·32	634
303	0·72	1·66	47·04	765
1351	0·16	2·22	46·48	742
				Mean $=702·4\times10^{-6}$

K = 0·001336.
A = 0·000557, or 2·34 per cent. of salt hydrolysed.

$\frac{N}{40}$ Potassium Cyanide (concentrations in $\frac{1}{200}$ gram-molecule per litre).

t.	C_2-x.	x.	$C-x$.	
0	4·73	0·00	97·40	
2	4·42	0·31	97·09	
5	4·11	0·62	96·78	$(1050)\times10^{-6}$
10	3·86	0·87	96·53	(893)
23	3·57	1·16	96·24	728
36	3·26	1·47	95·93	728
60	2·94	1·79	95·61	686
122	2·30	2·43	94·97	720
180	2·02	2·71	94·69	653
				Mean $=703\times10^{-6}$

K = 0·001328.
A = 0·000553, or 2·35 per cent. of salt hydrolysed.

Sodium Carbonate.

Experiments were made with $\frac{1}{5}$, $\frac{1}{10}$, $\frac{1}{20}$, and $\frac{1}{40}$ *molecular* normal solutions of sodium carbonate.

The titrations were made with the aid of phenol phthaleïn at the ordinary temperature of the laboratory. In this way the amount of standard acid added corresponded only to one half of the real concentration of the salt in hundredths of a gram-molecule per litre, as the solution becomes practically neutral when the unaltered sodium carbonate has been converted into sodium hydrogen carbonate. This would necessitate the doubling of

the apparent concentrations; but since the exact point of neutrality was difficult to observe, two series of experiments were made to eliminate as much as possible the experimental error and the sum of the apparent concentrations taken to represent C_2-x. Consequently, in the tables for sodium carbonate there are two extra columns (I. and II.) with the sum of the numbers contained in them given under the column C_2-x. The temperature at which all the experiments on sodium carbonate was made was 24°·2 C., and the coefficient of velocity k for sodium hydrate at this temperature is taken at 6·23.

$\frac{N}{5}$ (mol.) Sodium Carbonate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	19·00	19·00	38·00	0·00	48·70	
2	18·15	18·10	36·25	1·75	46·95	
4	17·40	17·27	34·67	3·33	45·37	$(150)\times10^{-6}$
8	16·55	16·65	33·20	4·80	43·90	129
12	15·95	15·99	31·94	6·06	42·64	138
20	15·15	15·15	30·30	7·70	41·00	135
30	14·72	14·74	29·46	8·54	40·16	112
50	13·23	13·26	26·49	11·51	37·19	136
85	11·80	11·95	23·75	14·25	34·45	136
155	10·10	9·97	20·07	17·93	30·77	141
						Mean $=132{\cdot}4\times10^{-6}$

K = 0·01738.
A = 0·00804, or 2·12 per cent. of salt hydrolysed.

$\frac{N}{10}$ (mol.) Sodium Carbonate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	9·40	9·40	18·80	0·00	48·70	
2	9·07	9·05	18·12	0·68	48·02	
4	8·85	8·10	16·95	1·85	46·85	$(625)\times10^{-6}$
8	7·85	7·60	15·45	3·35	45·35	815
12	7·30	7·25	14·55	4·25	44·45	839
16	6·95	6·90	13·85	4·95	43·75	854
20	6·60	6·62	13·22	5·58	43·12	880
24	6·40	6·35	12·75	6·05	42·65	874
32	5·82	6·08	11·90	6·90	41·80	885
66	5·12	5·10	10·22	8·85	40·12	741
						Mean $=841\times10^{-6}$

K = 0·01954.
A = 0·00596, or 3·17 per cent. of salt hydrolysed.

$\frac{N}{20}$ (mol.) Sodium Carbonate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	4·77	4·77	9·54	0·00	48·70	
2	4·30	4·33	8·63	0·91	47·79	
4	3·84	3·90	7·74	1·80	46·90	278×10^{-5}
8	3·44	3·50	6·94	2·60	46·10	247
12	3·01	3·18	6·19	3·35	45·35	281
16	2·90	2·96	5·86	3·68	45·02	255
32	2·47	2·25	4·72	4·82	43·88	243
40	2·05	2·07	4·12	5·42	43·28	266
62	1·52	1·60	3·12	6·42	42·28	283
92	1·22	1·24	2·46	7·08	41·62	265
						Mean $=265\times10^{-5}$

K = 0·02383.
A = 0·00465, or 4·87 per cent. of salt hydrolysed.

$\frac{N}{40}$ (mol.) Sodium Carbonate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	2·38	2·38	4·76	0·00	48·70	
2	1·95	2·25	4·20	0·56	48·14	
4	1·75	1·80	3·55	1·21	47·49	634×10^{-5}
8	1·35	1·53	2·88	1·88	46·82	676
12	1·22	1·23	2·45	2·31	46·39	698
16	1·10	1·17	2·27	2·49	46·21	613
20	1·02	1·07	2·09	2·67	46·03	579
28	0·75	0·85	1·60	3·16	45 54	665
56	0·49	0·41	0·90	3·86	44·84	656
						Mean $=646\times10^{-5}$

K = 0·02586.
A = 0·00338, or 7·10 per cent. of salt hydrolysed.

Potassium Phenate.

Carbolic acid or phenol is another well-known weak acid which forms a crystalline salt with potash. As an experiment with this salt seemed likely to be interesting, solutions of it were prepared by mixing equivalent quantities of solutions of potash and phenol of known strength and then diluting until solutions of the salt of the required concentration were obtained. Two sets of experiments were made; one with

$\frac{1}{10}$ and the other with $\frac{1}{50}$ normal solutions. The indicator used for titration was nitrophenol.

The temperature of the thermostat was 24°·1 C., and the coefficient of velocity for potash at this temperature was taken as 6·19. Each set of experiments was done in duplicate, the separate results being given in the columns I. and II. The mean of these is contained in the column C_2-x. In the case of the $\frac{1}{50}$ normal solution the concentrations are expressed in $\frac{1}{200}$ instead of $\frac{1}{100}$ gram-molecule per litre, as before.

$\frac{N}{10}$ Potassium Phenate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	9·62	9·62	9·62	0·00	48·70	
2	8·80	8·80	8·80	0·82	47·88	
4	8·30	8·20	8·25	1·37	47·33	$(133)\times10^{-5}$
6	8·03	8·00	8·01	1·61	47·09	107
8	7·81	7·77	7·79	1·83	46·87	101
10	7·66	7·60	7·63	1·99	46·71	95
12	7·45	7·43	7·44	2·18	46·52	96
16	7·09	7·09	7·09	2·53	46·17	99
22	6·75	6·71	6·73	2·89	45·81	97
30	6·20	6·10	6·15	3·47	45·23	109
						Mean $=101\times10^{-5}$

K = 0·00925.
A = 0·002936, or 3·05 per cent. of salt hydrolysed.

$\frac{N}{50}$ Potassium Phenate.

t.	I.	II.	C_2-x.	x.	$C-x$.	
0	3·90	3·90	3·90	0·00	97·40	
2	3·15	3·10	3·12	0·78	96·62	
4	2·78	2·80	2·79	1·11	96·29	567×10^{-5}
5	2·60	2·67	2·64	1·26	96·14	611
6	2·49	2·54	2·52	1·38	96·02	627
8	2·27	2·27	2·27	1·63	95·77	(704)
12	2·10	2·04	2·07	1·83	95·57	596
16	1·88	1·86	1·87	2·03	95·37	578
20	1·66	1·64	1·65	2·25	95·15	613
25	.....	1·46	1·46	2·44	94·96	616
30	.....	1·29	1·29	2·61	94·79	629
						Mean $=605\times10^{-5}$

K = 0·00939.
A = 0·001305, or 6·69 per cent. of salt hydrolysed.

Borax.

Several experiments were made with solutions of borax, but the results were by no means as satisfactory as could be desired. The chief difficulty seemed to be in the want of a suitable indicator. After trying about twenty I finally selected litmus as the one which gave the best results. Next to litmus came rosolic acid. I first of all prepared a solution of litmus of a certain purple tint to act as a guide or standard, and then I added acid to the solution under examination until it became of the same tint. I shall only give one series of experiments with a $\frac{1}{32}$ molecular normal solution of borax, so that some conception may be formed as to the amount of hydrolysis in solutions of borax.

The temperature of experiment was 24°·2 C., and the coefficient of velocity for sodium hydrate corresponding to this temperature is 6·23.

$\frac{N}{32}$ (mol.) Borax.

t.	C_2-x.	x.	$C-x$.	
0	5·85	0·00	48·70	
4	5·82	0·03	48·67	
8	5·72	0·13	48·57	$(30)\times10^{-6}$
30	5·55	0·30	48·40	(22)
188	4·10	1·75	46·95	120
1190	2·73	3·12	45·58	86
2885	1·40	4·45	45·25	95
4375	0·95	4·85	43·85	94
				Mean $= 99\times10^{-6}$

K = 0·00050.

A = 0·000738, or 0·92 per cent. of salt hydrolysed.

The Influence of Dilution on the Amount of Hydrolysis.

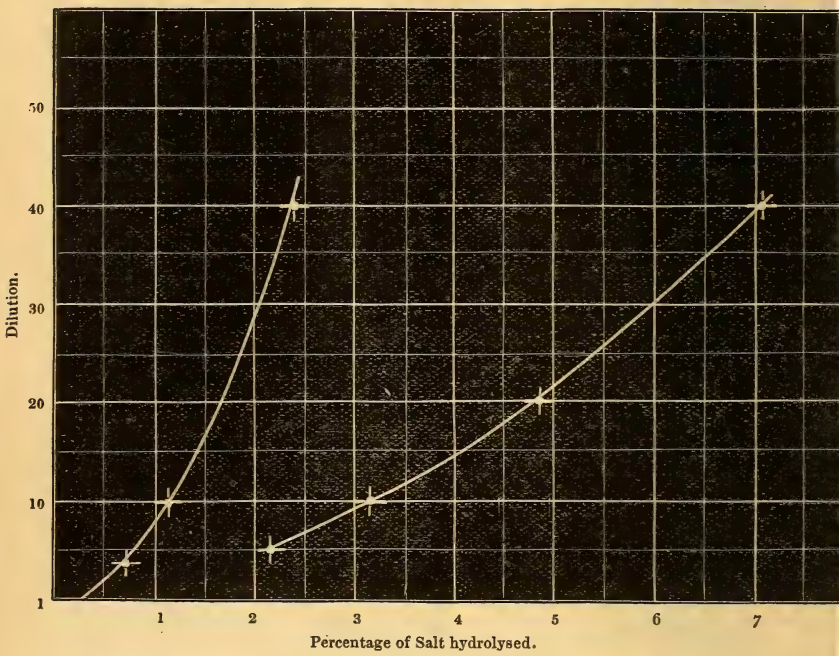
The table which follows contains the general results of the foregoing experiments and shows the effect of dilution on the amount of hydrolysis.

The first column gives the approximate concentration of the solution, the second the amount of free alkali in the solution in gram-molecules per litre, and the last the percentage amount of salt hydrolysed.

Concentration.	A.	Hydrolysis.
$\frac{N}{1}$ KCN	0·00296	0·31 per cent.
$\frac{N}{4}$ "	0·00168	0·72 "
$\frac{N}{10}$ "	0·00107	1·12 "
$\frac{N}{40}$ "	0·000557	2·34 "
$\frac{N}{5}$ (mol.)Na_2CO_3	0·00804	2·12 "
$\frac{N}{10}$ "	0·00596	3·17 "
$\frac{N}{20}$ "	0·00465	4·87 "
$\frac{N}{40}$ "	0·00338	7·10 "
$\frac{N}{10}C_6H_5OK$	0·00294	3·05 "
$\frac{N}{50}$ "	0·00131	6·69 "
$\frac{N}{32}$ (mol.)$Na_2B_4O_7$ ...	0·00074	0·92 "

A glance at the table will show that among the four substances examined the greatest amount of hydrolysis occurs in the case of sodium carbonate. The numbers cannot pretend to a very high degree of accuracy, chiefly on account of the difficulties in obtaining suitable indicators for the titration of the solutions, but the following regularity is easily discernible. *The amount of free alkali contained in the salt-solutions is proportional to the square root of the concentration of the salt.* This is, however, not strictly true, but more nearly expresses the truth the greater the dilution of the solution. A rough calculation on the numbers for the two most concentrated solutions of potassium cyanide shows that there is a deviation from the law of about 13 per cent., whilst for the less concentrated solutions the deviation is reduced to about 4 per cent. If the dilutions be plotted as ordinates against the percentage amount of salt hydrolysed as abscissæ, curves are obtained. Fig. 1 represents the curves for potassium cyanide and sodium carbonate. These curves enable us to see at a glance the percentage of salt hydrolysed at any given dilution. For example,

Fig. 1.



reading from the curve, there should be 1·65 per cent. of the potassium cyanide decomposed in a $\frac{1}{20}$ normal solution of that salt. If calculated from the above law, the amount of hydrolysis is 1·58 per cent.

Now if the salt itself were the cause of the saponification of the ester, the velocity of the reaction which is proportional to the amount of free base present would have been very nearly directly proportional to the concentration of the salt; but it has been found approximately proportional to the square root of the concentration, consequently the view that the salt itself produces the saponification is untenable.

The law which has just been enunciated is what we should expect from the theory; for if we again take the case of potassium cyanide, we get, neglecting the dissociation ratios as formerly,

$$KOH + HCN \rightleftharpoons KCN + HOH,$$

$$x \,.\, x = (C_2 - x)K\ ;$$

where C_2 is the initial concentration of the potassium cyanide, and x the fraction of it which has been hydrolysed. When x is very small compared with C_2, the above equation becomes

$$x = K_1 \sqrt{C_2}\ ;$$

that is to say, the amount of free potash is proportional to the square root of the concentration of the potassium-cyanide solution.

It has long been known that water decomposed certain salts, with formation of free acid and free base, but the amount of such decomposition has up to the present time only been measured in a few cases. It is true some guesses at it have occasionally been made, but they have proved rather unsatisfactory. For example, it has been supposed (see Ostwald's *Lehrbuch der allgem. Chemie*, vol. ii. p. 187, 2nd edit.), from measurements of the heat of neutralization of hydrocyanic acid by caustic soda, that a solution of sodium cyanide contains only one fifth of the salt as such, whilst the other four fifths are decomposed into free acid and free base.

The experiments which I have made on the velocity of reaction show that in a tenth-normal solution of potassium cyanide only about one per cent. of the salt is decomposed in the way indicated. The results which J. Thomsen (*Thermochemische Untersuchungen*, vol. i. p. 161) obtained on neutralizing one molecule of sodium hydrate with n molecules of hydrogen cyanide are as follows :—

n.	NaOH Aq, nHCN Aq.
$\frac{1}{2}$	13·68 heat units.
1	27·66 „
2	27·92 „

These numbers indicate that the amount of heat which is developed increases in the same proportion as the quantity of hydrogen cyanide added, until there are equivalent quantities of acid and base present. An excess of acid, then, produces only a very slight alteration in the value of the heat of neutralization.

Now manifestly this small increase in the heat of neutralization means that the first equivalent of hydrogen cyanide has almost all combined with the sodium hydrate. The cause of the incomplete combination is due of course to the mass action of the water. In short, it would seem that only a small fraction, presumably about one per cent., of the potassium cyanide is decomposed by the water into free acid and free base.

This corroborates the result which I have obtained by a totally different method.

A guess which H. Rose (*Jahresbericht*, 1852, p. 311) hazarded as to the amount of hydrolysis in an aqueous solution of borax is just as unsatisfactory. Rose supposed that

this substance in pretty dilute solution was almost entirely decomposed into acid and base; but the preceding experiments go to prove that in a $\frac{1}{32}$ molecular normal solution rather less than one per cent. is decomposed by the water. If the statement that the amount of free alkali in the solution is proportional to the square root of the concentration holds good for borax, then a solution in which the borax was completely hydrolysed would be almost infinitely dilute.

Rose has described a very interesting experiment which is intended to show the decomposition of borax by water. A tincture of litmus reddened with acetic acid is added to a concentrated solution of borax until the red colour has almost but not quite disappeared; the whole is then diluted with water, when the red colour changes to blue. I have repeated this experiment, and find that a solution prepared in the way Rose has indicated becomes distinctly blue on dilution. Joulin (*Bull. Soc. Chim. de Paris* [2] vol. xix. p. 344, 1873), however, could not observe this change of colour, and moreover has attempted to show that water exercises no decomposing influence at all on salts; but there is little doubt that he has been too hasty in coming to this conclusion, and that Rose, at least qualitatively speaking, was right.

Trisodium Phosphate.

A preliminary experiment with a $\frac{N}{50}$ solution of this salt showed that the velocity of reaction, on saponifying ethyl acetate, was singularly great when compared with what had been observed in the case of the other salt-solutions, and in fact closely approached that for a $\frac{1}{50}$ normal solution of caustic soda itself. This seemed to indicate that the solution under examination was almost entirely hydrolysed in the sense of the equation

$$Na_3PO_4 + HOH = Na_2HPO_4 + NaOH.$$

The formulæ which have hitherto been employed are of no use in this case, for they depend on the condition that A should be very small compared with x. Here A can in no case be neglected; consequently the equation (3)

$$A = \frac{K(C_2 - x)}{x}$$

is inapplicable.

The general equation

$$\frac{dx}{dt} = k(C_1 - x)(C - x)$$

becomes

$$\frac{dx}{dt} = K(C_2 - x)(C - x), \quad . \quad . \quad . \quad . \quad (8)$$

when we substitute for the concentration of the base that of the sodium phosphate.

Instead of K we may write $k\mu$, where μ is a factor which expresses the ratio of the amount of free alkali present to what would be present if the hydrolysis of one sodium atom was complete.

Equation (8), on integration, gives the solution

$$\frac{1}{C-C_2}\log\text{nat.}\frac{C_2-x_0}{C_2-x_1}-\frac{1}{C-C_2}\log\text{nat.}\frac{C-x_0}{C-x_1}=k\mu(t_1-t_0),$$

or

$$\log\frac{C_2-x_0}{C_2-x_1}-\log\frac{C-x_0}{C-x_1}=0{\cdot}4343\,k\mu(t_1-t_0)(C-C_2), \quad . \quad (9)$$

from which we can calculate μ at the time t_1.

In order to determine μ at the commencement, the different values of μ are plotted against the times, and the curve so obtained prolonged. The point at which it cuts the axis for the time $t=0$ gives the value of μ at the commencement.

Experiments have been made which show that Na_2HPO_4 is only slightly hydrolysed; so if we neglect this and assume that the equation

$$Na_3PO_4+HOH=Na_2HPO_4+NaOH$$

represents the *possible* quantity of caustic soda which can be formed in the solution, then 100μ represents the percentage amount of the caustic soda which *actually exists* in the solution.

The following experiments were made with a $\frac{1}{50}$ molecular normal solution of trisodium phosphate at 24°·2 C., at which temperature the coefficient of velocity of reaction for caustic soda is 6·28. The concentrations are expressed in $\frac{1}{200}$ of a gram-molecule per litre, and the employment of phenol phthaleïn enabled the titrations to be made pretty accurately.

$\frac{N}{50}$ (mol.) Trisodium Phosphate.

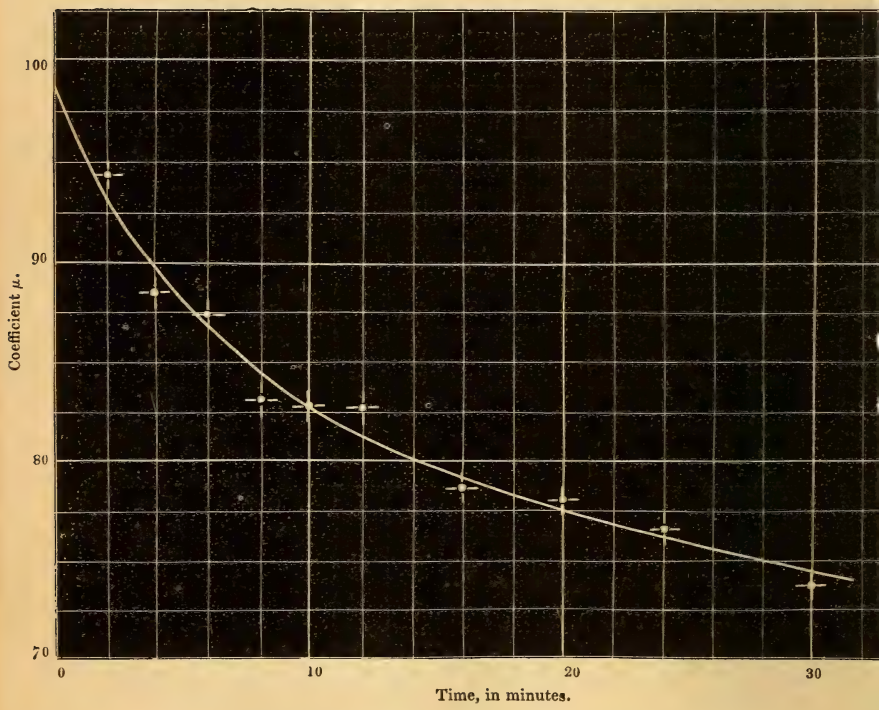
t.	I.	II.	C_2-x.	x.	$C-x$.	μ.
0	3·81	3·81	3·81	0·00	4·87	
2	2·93	2·95	2·94	0·87	4·00	0·945
4	2·41	2·45	2·43	1·38	3·49	0·882
6	2·06	2·03	2·04	1·77	3·10	0·873
8	1·82	1·77	1·79	2·02	2·85	0·831
10	1·58	1·55	1·56	2·25	2·62	0·827
12	1·35	1·40	1·37	2·44	2·43	0·827
16	1·12	1·14	1·13	2·68	2·19	0·788
20	0·91	0·94	0·93	2·88	1·99	0·780
24	0·79	0·80	0·79	3·02	1·85	0·764
30	0·63	0·66	0·64	3·17	1·70	0·738

If the equation

$$Na_3PO_4 + HOH = Na_2HPO_4 + NaOH$$

represented accurately the amount of hydrolysis, then μ at the commencement should be 1·00. A glance at the last column of the table shows that the equation must be nearly true. In order to find approximately the initial value of μ, a curve (fig. 2) has been drawn by plotting the values of μ as ordinates against the times t as abscissæ.

Fig. 2.



By referring to the curve it will be found that the initial value of μ is 0·98 at least; that is to say, at least 98 per cent. of one of the sodium atoms in Na_3PO_4 exists as free caustic soda in a $\frac{1}{50}$ molecular normal solution of the salt at 24°·2 C. In other words, although trisodium phosphate exists in the solid state, yet in dilute solution it is for the most part decomposed into hydrogen disodium phosphate and sodium hydrate. This result is in entire agreement with Berthelot's recent researches.

Allusion has already been made to the fact that hydrogen disodium phosphate is only slightly hydrolysed when dissolved in water. This salt behaves rather differently from the others. During the saponification the solution, which is at first alkaline, becomes neutral and then acid.

For the sake of comparison with trisodium phosphate, the following set of experiments was made with a $\frac{N}{20}$ (mol.) solution of hydrogen disodium phosphate at 24°·2 C. The solution was prepared from a sample of the salt obtained from Kahlbaum, and had a slightly alkaline reaction.

The titre of the solution during saponification was as follows :—

$\frac{N}{20}$ (mol.) Hydrogen Disodium Phosphate.

Time.	Titre.	
min.		
0	0·06	$\frac{1}{200}$ g.-mol. per litre (alkaline).
2	0·04	" "
5	0·00	Neutral.
32	0·06	$\frac{1}{100}$ g.-mol. per litre (acid).
120	0·10	" "
226	0·15	" "
380	0·17	" "
1380	0·30	" "
2815	0·41	" "
4500	0·52	" "

The titrations were made with phenol phthaleïn.

At the commencement the solution contained 0·0003 gram-molecule of free soda per litre.

The case is a very complicated one, but possibly the bulk of this alkalinity is due to the formation in the solution of trisodium phosphate ; there is still, however, a minute amount of free alkali in the solution, owing to the hydrolysis of hydrogen disodium phosphate. The following attempt has been made to measure it, but no stress must be laid on the results. I give the calculations here merely for the sake of comparison with trisodium phosphate, and to show that at the best there is not much free alkali in the solution. The calculations were made with the help of equations (6) and (7). It is evident, of course, that what we measure here is the quantity x. The initial concentrations of the salt and ester, expressed in hundredths of a gram-molecule per litre, are 4·76 and 48·76.

If we start at the point where the mixture is neutral we may construct the following table, from which we can calculate the quantity of free alkali in the solution at the point of apparent neutrality. This quantity, as has already been suggested, is perhaps due to the hydrolysis of hydrogen disodium phosphate; whilst the quantity of free alkali determined by direct titration is due to the presence of trisodium phosphate, formed according to the equation

$$2Na_2HPO_4 = Na_3PO_4 + NaH_2PO_4.$$

The influence of the dihydrogen sodium phosphate has been neglected altogether.

t.	C_2-x.	x.	$C-x$.	
0	4·76	0·00	48·70	
27	4·70	0·06	48·64	
115	4·66	0·10	48·60	64×10^{-8}
221	4·61	0·15	48·55	(86)
375	4·59	0·17	48·53	65
1375	4·46	0·30	48·40	59
2810	4·35	0·41	48·29	55
4495	4·24	0·52	48·18	54
			Mean =	59×10^{-8}

K = 0·00000236.
A = 0·000033, or 0·07 per cent. of salt hydrolysed.

The amount of free alkali determined by direct titration is 0·63 per cent., whilst that determined from the velocity of saponification, starting at the neutral point, is 0·07 per cent.; it is therefore evident that the total amount of free alkali in the solution is very small when compared with what is present in a solution of trisodium phosphate.

Sodium Acetate.

After having estimated the amount of hydrolysis in salts of strong bases with some of the weakest acids, it was thought desirable to extend the experiments a little and determine the amount of hydrolysis in a salt of a stronger acid, for example acetic acid. For this purpose a tenth normal solution of sodium acetate was prepared and investigated in the same manner as the salts of the weaker acids. The calculation of the results, however, was in this case much simplified, owing to the fact that the concentrations of the salt and ester did not alter much during the reaction, consequently

the mean values have been employed in calculating the characteristic constant.

If, in the equation (5),

$$\frac{dx}{dt} \cdot \frac{1}{C-x} \cdot \frac{1}{k} = \frac{K(C_2-x)}{x},$$

we substitute for C_2-x and $C-x$ their mean values 9·316 and 48·49, which were obtained from a series of experiments made at 24°·2 C., where $k=6·23$, we get:

$$\frac{dx}{d} \cdot \frac{1}{48·49} \cdot \frac{1}{6·23} = \frac{9·316\,K}{x},$$

which on integration gives the solution

$$6·23 \times 48·49 \times 9·316\,K = \frac{x_1^2 - x_0^2}{t_1 - t_0}.$$

Having got the characteristic constant K, equation (7) enables us to determine A, the amount of free soda in the solution at the beginning, expressed in gram-molecules per litre. The solution was titrated with the help of phenol phthaleïn.

In this case of course x, which is expressed in hundredths of a gram-molecule per litre, was measured directly. The values of x in the following table are the means of two concordant sets of experiments.

$\frac{N}{10}$ Sodium Acetate.

t.	C_2-x.	x.	$C-x$.	
0	9·52	0·000	48·70	
1224	9·46	0·060	48·64	
3952	9·455	0·065	48·635	
6882	9 385	0·135	48·565	$2·58 \times 10^{-6}$
21252	9·20	0·320	48·380	4·93
25550	9·20	0·320	48·380	4·06
34160	9·165	0·355	48·345	3·72
41290	9·14	0·380	48·320	3·51
Mean = 9·316.			Mean=48·49.	Mean=$3·76 \times 10^{-6}$.

K=0·0000000668.

A=0·00000798, or 0·008 per cent. of salt hydrolysed.

According to these measurements and calculations, it will be seen that in a tenth normal solution rather less than $\frac{1}{100}$ per cent. of sodium acetate is hydrolysed into free acid and

free base; thus,

$$CH_3COONa + HOH \rightleftharpoons CH_3COOH + NaOH.$$

It has already been stated that the presence of free weak acids has no measurable influence on the velocity with which the saponification takes place.

This is equally true in the case of sodium acetate, where acetic acid is one of the products of hydrolysis, and is also formed on the saponification of ethyl acetate. Arrhenius (*Zeits. f. physikal. Chemie*, vol. v. p. 2, 1890) has thoroughly investigated the change of the dissociation ratio of acetic acid on the addition of sodium acetate, and has shown that it may be regarded as *nil* in presence of large quantities of its salts.

By referring to the table it will be seen that the experiments on sodium acetate lasted for a considerable time, and it is conceivable that the water itself may have played an important part in the saponification of the ester. In order to test this a blank experiment was made with water and ethyl acetate under the same conditions as the experiment with the sodium acetate, and after the lapse of nearly three weeks the solution of the ester was only slightly acid. If, then, pure water, in virtue of its being electrolytically dissociated to a small extent, produces such an inappreciable effect, we can easily conjecture how infinitely slight this effect will be in presence of a strongly dissociated salt like sodium acetate.

The Influence of the Ester on the existing Equilibrium.

All the preceding deductions regarding the amount of hydrolysis in aqueous solutions of salts of strong bases with weak acids are based on the assumption that the equilibrium in aqueous solutions,

$$KCN + HOH \rightleftharpoons HCN + KOH,$$

is not disturbed by the presence of small quantities of ethyl acetate. To justify this assumption, I have made some experiments in which the concentration of the ester was varied, whilst the concentration of the salt remained nearly the same. Now, if the presence of the ester produced any change in the state of equilibrium, we should expect an alteration in the concentration of the ester to be accompanied by a corresponding variation in the amount of salt hydrolysed.

The following tables contain the results of experiments, on an approximately 0·1 normal solution of potassium cyanide, made at 25°·0 C., at which temperature $k = 6·54$.

I. Concentration of Ester = 0·4870 g.-mol. per litre.

t.	C_2-x.	x.	$C-x$.	
0	10·08	0·00	48·70	
2	9·70	0·38	48·32	
6	9·46	0·62	48·08	$(100)\times10^{-6}$
10	9·20	0·88	47·82	143
20	8·81	1·27	47·43	153
40	8·38	1·70	47·00	142
84	7·70	2·38	46·32	141
152	7·00	3·08	45·62	140
264	6·20	3·88	44·82	137
1484	2·90	7·18	41·52	139
				Mean = 142×10^{-6}

K=0·001305.
A=0·00114, or 1·13 per cent. KCN hydrolysed.

II. Concentration of Ester = 0·2005 g.-mol. per litre.

t.	C_2-x.	x.	$C-x$.	
0	10·38	0·00	20·05	
2	10·20	0·18	19·87	
6	9·99	0·39	19·66	$(27)\times10^{-6}$
12	9·77	0·61	19·44	(36)
27	9·41	0·97	19·08	39
63	8·90	1·48	18·57	40
131	8·26	2·12	17·93	42
243	7·67	2·71	17·34	39
1463	4·85	5·53	14·52	41
1683	4·56	5·82	14·23	42
				Mean = 40×10^{-6}

K=0·00151.
A=0·00124, or 1·20 per cent. KCN hydrolysed.

III. Concentration of Ester =0·1013 g.-mol. per litre.

t.	C_2-x.	x.	$C-x$.	
0	10·49	0·00	10·13	
2	10·40	0·09	10·04	
10	10·16	0·33	9·80	$(103)\times10^{-8}$
37	9·66	0·83	9·30	130
104	9·19	1·30	8·83	143
215	8·57	1·92	8·21	160
1435	6·40	4·09	6·04	164
1655	6·26	4·23	5·90	150
				Mean = 149×10^{-8}

K=0·00148.
A=0·00124, or 1·18 per cent. KCN hydrolysed.

The next small table contains the collected results of these experiments.

Conc. Ester.	K.	A.	KCN hydrolysed.
0·4870	0·00131	0·00114	1·13 per cent.
0·2005	0·00151	0·00124	1·20 „
0·1013	0·00148	0·00124	1·18 „

The numbers show that the concentration of the ester has no measurable influence on the amount of hydrolysis, since the figures in the last column do not arrange themselves in a series which is either gradually ascending or descending.

The differences between them are probably chiefly due to experimental error. The mean value is 1·17, and the greatest deviation from it is less than 5 per cent.

Résumé.—The general results of this investigation may briefly be stated as follows:—

1st. It is shown how the velocity with which salt-solutions saponify ethyl acetate may be utilized to determine the extent to which hydrolysis has taken place in aqueous solutions of salts of strong bases with weak acids.

2nd. The amount of hydrolysis has been measured in solutions of the following salts; and in $\frac{1}{10}$ molecular normal solutions between 24°–25° C. the amount of salt which is decomposed by the water is:—

Potassium cyanide	1·12 per cent.
Sodium carbonate	3·17 „
Potassium phenate	3·05 „
Borax (about)	0·5 „
Sodium acetate	0·008 „

3rd. When the salts are not hydrolysed to a great extent the amount of free alkali in the solutions is nearly proportional to the square root of the concentration.

4th. Trisodium phosphate can scarcely be said to exist in a $\frac{1}{50}$ molecular normal solution, as it is almost completely hydrolysed in the sense of the equation

$$Na_3PO_4 + HOH = Na_2HPO_4 + NaOH.$$

5th. The presence of small quantities of ethyl acetate in the solution does not materially disturb the equilibrium,

$$KCN + HOH \rightleftharpoons KOH + HCN.$$

University College, London.

XXXVII. *Suggestion as to a possible Source of the Energy required for the Life of Bacilli, and as to the Cause of their small Size.* By G. Johnstone Stoney, *M.A., D.Sc., F.R.S., Vice-President, Royal Dublin Society* *.

IN that part of the material universe which man's position in time and space, and the limitations of his senses, permit him to investigate, the Dissipation of Energy is so prevalent that instances of the reverse process can seldom be clearly traced out, though many such can be dimly seen. Under these circumstances, even possible instances, such as that dealt with in this paper, are instructive if they are of a kind to be fully understood. They are also important, for if the universe is permanent, there must be, or have been, or be about to be, parts of the universe where the Concentration of Energy is as largely predominant as its dissipation is within our experience.

Some bacilli, *e. g.* some of the nitrifying bacilli of the soil, are said to be sustained by purely mineral food, while they furnish ejecta which contain as much potential energy as the food, or more. If this be the case, they must be supplied with a considerable amount of energy to enable them to evolve protoplasm and the other organic compounds of which they consist, from these materials. Now many bacilli are so situated that this energy is certainly not obtained from sunshine, and it is suggested that it may be derived from the gases or liquids about them.

The average speed with which the molecules of air dart about is known to be nearly 500 metres per second—the velocity of a rifle-bullet; and the velocity of some of the molecules must be many times this, probably five, six, or seven times as swift. We do not know so much about the velocities of the molecules in liquids as of those in gases, but the phenomenon of evaporation and some others indicate that they are at least occasionally comparable with those of a gas. Accordingly, whether the microbe derive a part of its oxygen or other nourishment from the gases, or from the liquids about it, it is conceivable that ONLY THE SWIFTER MOVING MOLECULES can penetrate the microbe sufficiently far, or from some other cause are either alone or predominantly fitted to be assimilated by it.

Now if this be what is actually taking place, the adjoining air or liquid must become cooler through the withdrawal from

* From the Scientific Proceedings of the Royal Dublin Society, vol. viii. part i. Communicated by the Author.

it of its swiftest molecules ; and, in compensation, an amount of energy exactly equivalent to this loss of heat is imparted to the microbes and available for the formation within them of organic compounds.

It is further evident that if this be the source of energy upon which bacilli and cocci have to draw, the minuteness of their narrowest dimension will be of advantage—probably essential—to them. Presumably it would only be limited by such other necessary conditions as may forbid the diminution of size being carried beyond a certain point. The diameter of a bacillus is frequently as small as half or a third of a micron, which brings it tolerably well into the neighbourhood of some molecular magnitudes.

The transference of energy here suggested may be what occurs notwithstanding that it does not comply with the Second Law of Thermodynamics, which states that heat will not pass from a cooler to a warmer body, unless some adequate compensating event occurs, or has occurred, in connexion with the transference. This law represents what happens when vast numbers of molecular events (which are the real events of nature) admit of being treated statistically, and furnish an *average* result. It, therefore, has its limits : and the communication of energy from air to minute organisms which is described above, is an example of a process which is exempt from its operation ; since this transference is supposed to be brought about by a *discriminating* treatment of the molecules that impinge upon the bacillus of precisely the same kind as that which Maxwell pictured as made by his well-known demons. It therefore belongs to the recognized exception to the Second Law of Thermodynamics, viz., that which occurs in the few cases in which we can have under observation the special consequences of *selected* molecular events, instead of, as on all ordinary occasions, being only able to measure an *average* outcome from *all* the molecular events in the portion of matter we are examining.

If some bacilli—those which live on mineral food—obtain their whole stock of energy in the way here indicated, it may be presumed that all bacilli get at least a part of what they require in the same way.

Should the reader have any doubt as to whether the process here described is one of those that contradict the Second Law of Thermodynamics, he may satisfy himself on this head by the following considerations :—

Imagine a perfect heat-engine within an adiabatic envelope with some bacilli and an abundance of their mineral food, all

being at one temperature. If events take place as supposed above, the bacilli receive sufficient energy from the surrounding medium to enable them to assimilate their mineral food, and thereby to grow and multiply. Meanwhile the medium becomes cooler. We may then suppose that the new bacilli which have come into existence, and all the excreta, are used as fuel in the heat-engine, and that its refrigerator is as near as we please to being at the temperature to which the medium has been reduced. The combustion of the fuel may take the form of resolving the bacilli and excreta back into the mineral substances from which they had been evolved, except that these are now at the temperature of the combustion. Let us next reduce this temperature in the heat-engine to the temperature of the refrigerator. During this process a portion of the heat may be converted into mechanical energy; and at the end of the process everything within the enclosure is in the same state as at the beginning, with the sole exceptions that some of the bodies within the enclosure are now at a lower temperature than at the beginning, and that the heat which they have lost has been converted into mechanical energy.

It thus appears that the contents of the adiabatic envelope may be regarded as a heat-engine, all the parts of which start at a certain temperature, and which yields mechanical energy, while the only other change is that some of its parts are cooled to a lower temperature. This contradicts the Second Law of Thermodynamics as formulated by Lord Kelvin, if we leave the word "inanimate" out of his enunciation. His statement of the axiom is:—"It is impossible by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects." It is legitimate here to omit the word "inanimate," as its insertion merely means that cases of exception to the law may be met with in the organic world; and if this be stated it will need to be added that cases of exception may also be found among inorganic processes: the correct statement being that the law does not apply to *individual* molecular events, and that therefore it need not be obeyed in the cases, whether organic or inorganic, in which any observable effect is the outcome of one-sided molecular events.

It should be borne in mind that the heat of a given portion of matter is the energy * of motions of and within its molecules;

* The energy here spoken of may be partly potential: in fact while motion is going on, the "energy of the motion," or a part of it, usually fluctuates between being kinetic and potential.

not necessarily of all such motions, but of those among them which are capable of restoring energy to the parts of the molecule carrying electra (see Stoney on "Double Lines in Spectra," Scientific Transactions of the Royal Dublin Society, vol. iv. part xi.) whenever the motion of the electron has transferred energy from the molecule to the æther. As fulfilling this criterion we are probably to include all irrotational motions within the molecules, and we must also include relative motions of the molecules—all of them indeed if time enough be allowed for turmoil within a fluid to subside. It does *not* include any motion which the molecules have in common, as in wind, or in the rotation of a wheel.

When these circumstances are taken into account, it is obvious that the energy of the heat-motions of an individual molecule undergoes rapid fluctuations, while there may be a definite *average* of the energy of these motions, whether estimated by what happens in an individual molecule over a sufficiently long period of time, or when estimated by what occurs simultaneously in all the molecules of a body. In other words, the motions of an individual molecule do not from instant to instant conform to the Second Law of Thermodynamics, although the law may apply both to the average of the motions of a single molecule taken over a long period of time, and to the average of the simultaneous motions of vast multitudes of associated molecules. As regards *molecular* motions (the motions within a solid, or motions within a fluid that do not produce currents in the fluid), the millionth of one second is a long period.

XXXVIII. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETIZATION OF IRON RINGS SLIT IN A RADIAL DIRECTION. BY H. LEHMANN.

THE chief results of the present research may be summed up in the following principles, which hold for an imperfectly closed ferromagnetic ring, the radius of which is large in comparison with the radius of the section:—

1. The demagnetizing factor, or the factor which, multiplied by the mean magnetization, gives the mean factor of the demagnetizing force, is constant up to about half the saturation.

2. The coefficient of dispersion (*Streuungs-coefficient*), the ratio of the mean induction to that in the slit, is constant up to half saturation.

3. The region of the dispersion of the lines of force is limited essentially to the vicinity of the slit, and is narrower as the magnetization increases.

4. The coefficient of dispersion is independent of the radius of the ring; in regard to its constancy (2), it only depends on the

relative width of the ring d/r. The empirical expression for this dependence is a linear one of the form

$$1+h\frac{d}{r};$$

where h is a constant which, for the Swedish iron investigated, has the value 7, and will presumably have values differing but little from this in the case of other ferromagnetic metals. This will probably be the case more especially in the kinds of iron used in technical processes.

5. When the empirical constant h is known, the factor of demagnetization can be calculated from the geometrical dimensions of the system by the formula

$$\overline{\mathrm{N}}=\frac{2d}{\left(\rho-\frac{d}{2\pi}\right)\left(1+h\frac{d}{r}\right)},$$

in which ρ is the radius of the ring, r that of the section, and d the width of the slit. This formula holds with the same limitation as (1), (2), and (4), that is, up to demisaturation. In general the equation holds,

$$\overline{\mathrm{N}}=\frac{2d}{\left(\rho-\frac{d}{2\pi}\right)}\cdot\frac{1}{\nu},$$

in which ν is the factor of dispersion.

6. For high magnetizing values the factor of demagnetization approaches the limiting value

$$\mathrm{N}\,\infty=2\frac{(d+r-\sqrt{d^2+r^2})}{\rho-\frac{d}{2\pi}}.$$

The previous results may find an approximate application even in imperfect magnetic circuits of complicated shapes.—Wiedemann's *Annalen*, No. 3, 1893.

THE SPECIFIC HEAT OF LIQUID AMMONIA.

BY C. LUDEKING AND J. E. STARR.

The specific heat of liquid ammonia, though it has often been the subject of calculation in development of theory and practice, has not yet been satisfactorily determined experimentally, if we except the work of Regnault. His results, however, were unfortunately lost during the Paris Commune. He assumed the specific heat to be 0·799. Since then the interest in this constant has very considerably increased through the rapid development of the artificial ice industry. Generally the specific heat has been taken at unity. Thus De Volson Wood in his 'Thermodynamics,' page 337, recommends this value "until the experimental value is determined."

It was our good fortune to have ready access to all the means necessary for executing the somewhat laborious experiments involved, and we take this opportunity to present briefly the

results of our work. The liquid ammonia used in the experiments was found on examination to contain 0·3 per cent. of moisture and on spontaneous evaporation to leave only a trace of residue. The impurities were therefore of no consequence in influencing the result to the limit of accuracy intended.

Of this liquid ammonia 10·01 grams were introduced into a small steel cylinder of 16·122 c.c. capacity, stoppered by a steel screw. The mode of filling was quite simple. After cooling the cylinder in a bath of the liquid ammonia itself and while still immersed, it was possible to pour it brimful by means of a beaker. The steel screw stopper, also previously cooled, was then inserted and drawn almost tight. On then removing the cylinder from the cooling bath, the liquid contents gradually expanded and escaped in quantity proportional thereto, and besides a very small vapour space was allowed to form as is indicated in the experimental data. Then the stopper was driven tight. Thus the error in the result due to the latent heat of condensation of vapour of ammonia in the course of the experiments was reduced to a minimum and rendered, as will be seen, almost inappreciable in its influence.

The cylinder was perfectly free from leakage and remained constant in weight during each series of determinations. It was suspended in the drum of a Regnault apparatus heated by the vapour of carbon disulphide. The entire mode of procedure was in all details that commonly used in the Regnault method. After the cylinder had been heated for about six hours, it was dropped into a brass calorimeter whose water value was 1·36 cal. and which contained 150 grams of water. In each experiment it required very nearly two minutes to raise the calorimeter to its maximum temperature. The influence of loss by radiation was reduced to a minimum by the Rumford manipulation. The thermometers used were standardized, carefully compared, and read to hundredths of a degree by means of a magnifying lens. The experiments were conducted sufficiently far from the critical temperature, which according to Vincent and Chappuis is 131° C.

The following are the data of Experiment 1 :—

Weight of steel cylinder and ammonia. ..	81·008 grams.
Weight of steel cylinder	70·998 „
Weight of ammonia	10·01 „

The specific gravity of liquid ammonia being 0·656, the volume of 10·01 grams is 15·26 c.c.

Total water value of calorimeter, thermometer, and water	151·76 cal.
Water value of steel cylinder	8·34 cal.
Temperature of air	25°·4 C.
Temperature of steel cylinder	46°·51 C.
Temperature of calorimeter after immersion	26°·69 C.
Temperature of calorimeter before immersion	24°·44 C.
Rise in temperature	2°·25 C.

Thus 341·46 cal. were given off by the cylinder in cooling 19°·82 or 17·23 cal. for one degree. Of this 8·34 cal. are due to the steel cylinder itself, leaving 8·89 cal. for 10·01 grams of liquid ammonia or 0·888 per gram = specific heat. In a second and third experiment the values 0·897 and 0·896 were obtained. The determination of the specific heat of liquid ammonia would be influenced, as stated, by the latent heat of condensation of part of the small quantity of vapour present, when the cylinder cools in the calorimeter. This would to a degree be neutralized by the contraction of the liquid ammonia itself in the cooling and the consequent formation of more vapour space.

It seemed desirable to ascertain the influence of these factors collectively by experiment. For this purpose specific heat determinations were made in a way somewhat different from the ordinary. The steel cylinder was cooled in an iron shell in melting ice, instead of being heated, and then introduced into the warm calorimeter water. The mode of precedure was in detail similar to that described above, and we will therefore only give our results. In three experiments the values 0·878, 0·863, and 0·892 were obtained. They are a trifle lower in their average than the results obtained by the ordinary method. It is reasonable to assume that they are somewhat low, while as stated the other results are presumably somewhat high; and in order to arrive at the specific heat of this substance nearest the true value from our experimental evidence, we will take the average of our six values, viz.:

$$\left.\begin{array}{l}0{\cdot}888\\0{\cdot}897\\0{\cdot}896\end{array}\right\}\text{1st series,}\qquad\left.\begin{array}{l}0{\cdot}878\\0{\cdot}863\\0{\cdot}892\end{array}\right\}\text{2nd series,}$$

and state it as being = 0·8857.

We beg herewith to acknowledge our obligations to Chancellor W. S. Chaplin and Prof. Wm. B. Potter for kindly placing the laboratories under their charges at our disposal.—*Silliman's Journal*, March 1893.

ON THE OFFICIAL TESTING OF THERMOMETERS.

BY H. F. WIEBE.

In the year 1885 the Imperial Standards Commission undertook on a large scale the official testing of thermometers which is of such great importance both in science and in practice; while previously only a few institutions, such as the Naval Office, had occupied themselves to a limited extent with the investigation of thermometers. These official testings were transferred to the recently established Physical Technical Imperial Institute, to which since then a great number of thermometers have every year been sent for investigation. (In Ilmenau there is a branch for these testings.) Through the great progress which has been made since Jena glass has been used for thermometers, it has been possible to undertake a permanent guarantee for the results obtained in such testing; and from the uniformity of this glass the thermometric constants, once determined, may be universally adopted. The testing takes

place in two ways—either by comparison with a standard thermometer at different temperatures, or by calibration and determination of the thermometric constants. The comparison of the thermometers is made between 0° and 50° in water-baths; above 50° in boiling-point apparatus with reversing condensers, in which liquids of various boiling-points are used for the determinations. The following liquids were found to be especially suitable:—

	Boiling-point.		Boiling-point.
Chloroform	60·6°	Toluole	109·4°
Methylic alcohol	64·5	Isobutylic acetate	114·1
Methylic ethylic alcohol 1 : 1	69·8	Paraldehyde	124·6
Methylic ethylic alcohol 3 : 7	72·4	Amylic alcohol	129·8
Ethylic alcohol	78·1	Xylole	139·4
Ethylic propylic alcohol 16 : 3	79·8	Amylic acetate	140·0
Benzole	79·9	Bromoform	148·9
Ethylic propylic alcohol 7 : 4	82·2	Turpentine ....about	160·0
Isobutylic bromide	87·4	Aniline	184·3
Ethylic propylic alcohol 1 : 8	91·5	Dimethylamine	194·0
Propylic alcohol	96·0	Methylic benzoate	199·3
Isobutylic alcohol	105·7	Toluidine	199·5
		Ethylic benzoate	212·3
		Chinoline	235·9
		Amylic benzoate	259·5
		Glycerine	290·1
		Diphenylamine	301·9

By boiling various liquids under diminished pressure constant temperatures may be obtained, and this method is also used in the Imperial Institute between temperatures of 50° and 140° (compare *Beiblätter*, vol. xvi. p. 507). The statement as to the correction refers to thermometers completely immersed, and corrections must be introduced afterwards for the projecting thread (compare also Rimbach, *Beiblätter*, vol. xvi. p. 417).

The second kind of investigation which is indispensable for accurate instruments consists in calibrating them, determining the distance of the fixed points, &c. The methods for this are described in the *Trav. et Mém. du Bureau international*, &c. The position of the freezing-point at $t°$ is, according to Böttcher,

$$E_t = E_{100} + 0{\cdot}0055\,(100-t) + 0{\cdot}0_6 8\,(100-t^2).$$

The reduction of the data of the mercurial thermometer of Jena glass 16''' to those of the air-thermometer, according to Wiebe and Böttcher, are calculated from the formula

$$\delta = -0{\cdot}0_4 280\,(100-t) - 0{\cdot}0_6 299\,(100-t^2),$$

in which t stands for degrees of the mercury-thermometer, δ the reduction to the air-thermometer (see *Beiblätter*, vol. xvi. p. 352).

For testing the thermometers at low temperatures mixtures of salts are used to −33°; for still lower temperatures mixtures of solid carbonic acid with mixtures of alcohol and water in various proportions (to −78°·8). Above 300° baths of fused nitre are used; the best is a mixture of potassium and sodium nitrates in equal parts melting at 230°. Thermometers of Jena glass filled with nitrogen may be used after a previous continuous heating to about 480° to 450°.—*Zeitschrift für analyt. Chemie*, vol. xxx. p. 1 (1891); *Beiblätter der Physik*, vol. xvii. p. 100.

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XXXIX. *Gratings in Theory and Practice**. *By* HENRY A. ROWLAND †.

PART I.

IT is not my object to treat the theory of diffraction in general, but only to apply the simplest ordinary theory to gratings made by ruling grooves with a diamond on glass or metal. This study I at first made with a view of guiding me in the construction of the dividing-engine for the manufacture of gratings, and I have given the present theory for years in my lectures. As the subject is not generally understood in all its bearings I have written it for publication.

Let p be the virtual distance reduced to *vacuo* through which a ray moves. Then the effect at any point will be found by the summation of the quantity

$$A \cos b(p - Vt) + B \sin b(p - Vt),$$

in which $b = \frac{2\pi}{l}$, l being the wave-length, V is the velocity reduced to *vacuo*, and t is the time. Making $\theta = \tan^{-1}\frac{A}{B}$,

* Reprinted from a separate copy from the 'Astronom. and Astero-Physics' for February communicated by the Author.

† I am much indebted to Dr. J. S. Ames for looking over the proofs of this paper and correcting some errors. In the paper I have, in order to make it complete, given some results obtained previously by others, especially by Lord Rayleigh. The treatment is, however, new, as well as many of the results. My object was originally to obtain some guide to the effect of errors in gratings, so that in constructing my dividing-engine I might prevent their appearance if possible.

we can write this

$$\sqrt{A^2+B^2}\sin[\theta+b(p-Vt)].$$

The energy or intensity is proportional to (A^2+B^2).

Taking the expression

$$(A+iB)e^{-ib(p-Vt)},$$

when $i=\sqrt{-1}$, its real part will be the previous expression for the displacement. Should we use the exponential expression instead of the circular function in our summation, we see that we can always obtain the intensity of the light by multiplying the final result by itself with $-i$ in place of $+i$, because we have

$$(A+iB)e^{-ib(p-Vt)}\times(A-iB)e^{ib(p-Vt)}=A^2+B^2.$$

In cases where a ray of light falls on a surface where it is broken up, it is not necessary to take account of the change of phase at the surface, but only to sum up the displacement as given above.

In all our problems let the grating be rather small compared with the distance of the screen receiving the light, so that the displacements need not be divided into their components before summation.

Let the point x', y', z' be the source of light, and at the point x, y, z let it be broken up and at the same time pass from a medium of index of refraction I' to one of I. Consider the disturbance at a point x'', y'', z'' in the new medium. It will be

$$e^{-ib(I\rho+I'p-Vt)},$$

where

$$\rho^2=x''^2+y''^2+z''^2+x^2+y^2+z^2-2(xx''+yy''+zz''),$$

$$p^2=x'^2+y'^2+z'^2+x^2+y^2+z^2-2(xx'+yy'+zz').$$

Let the point x, y, z be near the origin of coordinates as compared with x', y', z' or x'', y'', z'', and let α, β, γ and α', β', γ' be the direction-cosines of ρ and p. Then, writing

$$R=I'\sqrt{x'^2+y'^2+z'^2}+I\sqrt{x''^2+y''^2+z''^2},$$

$$\lambda=I\alpha+I'\alpha',$$

$$\mu=I\beta+I'\beta',$$

$$\nu=I\gamma+I'\gamma',$$

we have, for the elementary displacement,

$$e^{-ib[R-Vt-\lambda x-\mu y-\nu z+\kappa r^2]};$$

where
$$\kappa=\tfrac{1}{2}\left[\frac{\mathrm{I}'}{\sqrt{x'^2+y'^2+z'^2}}+\frac{\mathrm{I}}{\sqrt{x''^2+y''^2+z''^2}}\right],$$
and
$$r^2=x^2+y^2+z^2.$$

This equation applies to light in any direction. In the special case of parallel light, for which $\kappa=0$, falling on a plane grating with lines in the direction of z, one condition will be that this expression must be the same for all values of z.

Hence
$$\nu=0.$$

If N is the order of the spectrum and a the grating-space, we shall see further on that we also have the condition
$$ba\mu=2\pi\mathrm{N}=\frac{2\pi a}{l}\mu.$$

The direction of the diffracted light will then be defined by the equations
$$\alpha'^2+\beta'^2+\gamma'^2=0,$$
$$\mathrm{I}\gamma+\mathrm{I}'\gamma'=0,$$
$$\mathrm{I}\beta+\mathrm{I}'\beta'=\frac{l}{a}\mathrm{N}.$$

Whence
$$\mathrm{I}'\alpha'=\mathrm{I}\sqrt{\alpha^2+2\frac{l}{\mathrm{I}a}\mathrm{N}\beta-\frac{l^2\mathrm{N}^2}{\mathrm{I}^2a^2}},$$
$$\mathrm{I}'\beta'=\frac{l}{a}\mathrm{N}-\mathrm{I}\beta,$$
$$\mathrm{I}'\gamma'=-\mathrm{I}\gamma.$$

In the ordinary case, where the incident and diffracted rays are perpendicular to the lines of the grating, we can simplify the equations somewhat.

Let ϕ be the angle of incidence and ψ of diffraction as measured from the positive direction of X.
$$\lambda=\mathrm{I}'\cos\phi+\mathrm{I}\cos\psi,$$
$$\frac{l}{a}\mathrm{N}=\mu=\mathrm{I}'\sin\phi+\mathrm{I}\sin\psi,$$
$$b=\frac{2\pi}{l},$$
where l is the wave-length *in vacuo*.

In case of the reflecting-grating $\mathrm{I}=\mathrm{I}'$, and we can write
$$\lambda=\mathrm{I}\{\cos\phi+\cos\psi\},$$
$$\frac{l}{a}\mathrm{N}=\mu=\mathrm{I}\{\sin\phi+\sin\psi\}.$$

This is only a very elementary expression, as the real value would depend on the nature of the obstacle, the angles, &c., but it will be sufficient for our purpose.

The disturbance due to any grating or similar body will then be very nearly

$$\iint e^{-ib[\mathrm{R}-\mathrm{V}t-\lambda x-\mu y-\nu z+\kappa(x^2+y^2+z^2)]}ds,$$

where ds is a differential of the surface. For parallel rays, $\kappa=0$.

Plane Gratings.

In this case the integration can often be neglected in the direction of z, and we can write for the disturbance in case of parallel rays,

$$e^{-ib(\mathrm{R}-\mathrm{V}t)}\iint e^{-ib[-\lambda x-\mu y]}ds.$$

Case I.—Simple Periodic Ruling.

Let the surface be divided up into equal parts, in each of which one or more lines or grooves are ruled parallel to the axis of z.

The integration over the surface will then resolve itself into an integration over one space, and a summation with respect to the number of spaces. For in this case we can replace y by $na+y$, where a is the width of a space, and the displacement becomes

$$e^{-ib(\mathrm{R}-\mathrm{V}t)}\Sigma e^{+ib\mu an}\iint e^{+ib(\lambda x+\mu y)}ds;$$

but

$$\Sigma_0^{n-1}e^{+ib\mu an}=e^{+i\frac{n-1}{2}ba\mu}\frac{\sin n\dfrac{ba\mu}{2}}{\sin\dfrac{ba\mu}{2}}.$$

Multiplying the disturbance by itself with $-i$ in place of $+i$, we have for the light intensity,

$$\left\{\frac{\sin n\dfrac{ba\mu}{2}}{\sin\dfrac{ba\mu}{2}}\right\}^2\left[\int e^{-ib(\lambda x+\mu y)}ds\right]\left[\int e^{+ib(\lambda x+\mu y)}ds\right].$$

The first term indicates spectral lines in positions given by the equation

$$\sin\frac{ba\mu}{2}=0,$$

with intensities given by the last integral. The intensity of the spectral lines then depends on the form of the groove as

given by the equation $x=f(y)$ and upon the angles of incidence and diffraction. The first factor has been often discussed, and it is only necessary to call attention to a few of its properties.

When $ba\mu=2\pi N$, N being any whole number, the expression becomes n^2. On either side of this value the intensity decreases until $nba\mu'=2\pi N$, when it becomes 0.

The spectral line then has a width represented by $\mu'-\mu''=2\frac{\mu}{n}$ nearly; on either side of this line smaller maxima exist too faintly to be observed. When two spectral lines are nearer together than half their width they blend and form one line. The defining power of the spectroscope can be expressed in terms of the quotient of the wave-length by the difference of wave-length of two lines that can just be seen as divided. The defining power is then

$$nN^*=na\frac{\mu}{l}.$$

Now na is the width of the grating. Hence, using a grating at a given angle, the defining power is independent of the number of lines to the inch and only depends on the width of the grating and the wave-length. According to this, the only object of ruling many lines to the inch in a grating is to separate the spectra so that, with a given angle, the order of spectrum shall be less.

Practically the gratings with few lines to the inch are much better than those with many, and hence have *better* definition at a given angle than the latter except that the spectra are more mixed up and more difficult to see.

It is also to be observed that the defining power increases with shorter wave-lengths, so that it is three times as great in the ultra-violet as in the red of the spectrum. This is of course the same with all optical instruments such as telescopes and microscopes.

The second term which determines the strength of the spectral lines will, however, give us much that is new.

First let us study the effect of the shape of the groove on the brightness. If N is the order of the spectrum and a the grating-space, we have

$$\mu=1(\sin\phi+\sin\psi)=\frac{Nl}{a},$$

since $\sin\frac{ba\mu}{2}=0$,

* An expression of Lord Rayleigh's.

and the intensity of the light becomes proportional to

$$\left[\iint e^{i2\pi\left(\frac{\lambda}{l}x+\frac{N}{a}y\right)}ds\right]\left[\iint e^{-i2\pi\left(\frac{\lambda}{l}x+\frac{N}{a}y\right)}ds\right].$$

It is to be noted that this expression is not only a function of N but also of l, the wave-length. This shows that the intensity in general may vary throughout the spectrum according to the wave-length, and that the sum of the light in any one spectrum is not always white light.

This is a peculiarity often noticed in gratings. Thus one spectrum may be almost wanting in the green, while another may contain an excess of this colour; again, there may be very little blue in one spectrum, while very often the similar spectrum on the other side may have its own share and that of the other one also. For this reason I have found it almost impossible to predict what the ultra-red spectrum may be, for it is often weak even where the visible spectrum is strong.

The integral may have almost any form, although it will naturally tend to be such as to make the lower orders the brightest when the diamond rules a single and simple groove. When it rules several lines or a compound groove, the higher orders may exceed the lower in brightness, and it is mathematically possible to have the grooves of such a shape that, for given angles, all the light may be thrown into one spectrum.

It is not uncommon, indeed very easy, to rule gratings with immensely bright first spectra, and I have one grating where it seems as if half the light were in the first spectrum on one side. In this case there is no reflexion of any account from the grating held perpendicularly: indeed, to see one's face the plate must be held at an angle, in which case the various features of the face are seen reflected almost as brightly as in a mirror but drawn out into spectra. In this case all the other spectra and the central image itself are very weak.

In general it would be easy to prove from the equation that want of symmetry in the grooves produces want of symmetry in the spectra—a fact universally observed in all gratings, and one which I generally utilize so that the light may be concentrated in a few spectra only.

Example 1.—Square Grooves.

When the light falls nearly perpendicularly on the plate, we need not take the sides into account but only sum up the surface of the plate and the bottom of the groove. Let the depth be X and the width equal to $\frac{a}{m}$.

The intensity then becomes proportional to

$$\frac{1}{N^2}\sin^2\pi\frac{N}{m}\sin^2\pi\frac{\lambda}{l}X.$$

This vanishes when

$$N=m,\ 2m,\ 3m,\ \&c.\ ;$$

or

$$\frac{\lambda X}{l}=0,\ 1,\ 2,\ 3,\ \&c.$$

The intensity of the central light, for which $N=0$, will be

$$\frac{\pi^2}{m^2}\sin^2\left(\pi\frac{\lambda}{l}X\right).$$

This can be made to vanish for only one angle for a given wave-length. Therefore, the central image will be coloured and the colour will change with the angle, an effect often observed in actual gratings. The colour ought to change, also, on placing the grating in a liquid of different index of refraction, since λ contains I, the index of refraction.

It will be instructive to take a special case, such as light falling perpendicularly on the plate. For this case,

$$\phi=0,\ \lambda=I(1+\cos\psi),\ \text{and}\ \mu=I\sin\psi=\frac{Nl}{a}.$$

Hence

$$\lambda=I\left\{1+\sqrt{1-\left(\frac{Nl}{aI}\right)^2}\right\}.$$

The last term in the intensity will then be

$$\sin^2\left\{\pi XI\left[\frac{1}{l}+\sqrt{\frac{1}{l^2}-\left(\frac{N}{aI}\right)^2}\right]\right\}.$$

As an example, let the green of the second order vanish. In this case, $l=\cdot00005$. $N=2$. Let $a=\cdot0002$ centim., and $I=1$.

Then $$X[20000+\sqrt{(20000)^2-(10000)^2}]=n.$$

Whence

$$X=\frac{n}{37300},$$

where n is any whole number. Make it 1.

Then the intensity, as far as this term is concerned, will be as follows :—

	Minima where Intensity is 0. Wave-lengths.		Maxima where Intensity is 1. Wave-lengths.		
1st spec....	·0000526	·0000268	·0001000	·00003544	·00002137
2nd „ ...	·0000500	·0000266	·0000833	·00003463	·00002119
3rd „ ...	·0000462	·0000263	·0000651	·00003333	·00002089
4th „ ...	·0000416	·0000259	·0000499	·00003169	·00002050
5th „ ...	&c.	&c.	&c.	&c.	&c.

The central light will contain the following wave-lengths as a maximum:—

·0001072, ·00003575, ·0000214, &c.

Of course it would be impossible to find a diamond to rule a rectangular groove as above, and the calculations can only be looked upon as a specimen of innumerable light distributions according to the shape of groove.

Every change in position of the diamond gives a different light distribution, and hundreds of changes may be made every day and yet the same distribution will never return, although one may try for years.

Example 2.—Triangular Groove.

Let the space a be cut into a triangular groove, the equations of the sides being $x=-cy$ and $x=c'(y-a)$, the two cuttings coming together at the point $y=u$. Hence we have $-cu=c'(u-a)$, and $ds=dy\sqrt{1+c^2}$, or $dy\sqrt{1+c'^2}$. Hence the intensity is proportional to

$$l^2\left\{\frac{1+c^2}{(\mu-c\lambda)^2}\sin^2\frac{\pi u(\mu-c\lambda)}{l}+\frac{1+c'^2}{(\mu+c'\lambda)^2}\sin^2\frac{\pi(a-u)(\mu+c'\lambda)}{l}\right.$$

$$+\frac{\sqrt{(1+c^2)(1+c'^2)}}{(\mu-cy)(\mu+c'\lambda)}\sin\frac{\pi u(\mu-c\lambda)}{l}\sin\frac{\pi(a-u)(\mu+c'\lambda)}{l}$$

$$\left.\cos\frac{\pi}{l}\left[(\mu+c'\lambda)(a-u)-n(\mu-c\lambda)\right]\right\}$$

This expression is not symmetrical with respect to the normal to the grating, unless the groove is symmetrical, in which case $c=c'$ and $u=\frac{a}{2}$.

In this case, as in the other, the colours of the spectrum are of variable intensity, and some of them may vanish as in the first example, but the distribution of intensity is in other respects quite different.

Case II.—Multiple Periodic Ruling.

Instead of having only one groove ruled on the plate in this space a, let us now suppose that a series of similar lines are ruled.

We have, then, to obtain the displacement by the same expression as before, that is

$$\frac{\sin n\dfrac{ba\mu}{2}}{\sin\dfrac{ba\mu}{2}}\int e^{ib(\lambda n+\mu y)}ds,$$

except that the last integral will extend over the whole number of lines ruled within the space a.

In the spaces a let a number of equal grooves be ruled commencing at the points $y=0$, y_1, y_2, y_3, &c., and extending to the points w, y_1+w, y_2+w, &c. The surface integral will then be divided into portions from w to y_1, from y_1+w to y_2, &c., on the original surface of the plate for which $x=0$, and from w to 0, from y_1+w to y_1, &c., for the grooves.

The first series of integrals will be

$$\int e^{ib\mu y}dy=\left\{\frac{1}{ib\mu}\right\}\{-e^{ib\mu w}+e^{ib\mu y_1}-e^{ib\mu(y_1+w)}+e^{ib\mu y_2}-\&c.\}$$

$$=\frac{1}{ib\mu}\{-e^{ib\mu w}+(1-e^{ib\mu w})(e^{ib\mu y_1}+e^{ib\mu y_2}+\&c.)+e^{ib\mu a}\}.$$

But $e^{ib\mu a}=1$ since $b\mu a=0$ for any maximum, and thus the integral becomes

$$\frac{1-e^{ib\mu w}}{ib\mu}\{1+e^{ib\mu y_1}+e^{ib\mu y_2}+\&c.\}.$$

The second series of integrals will be

$$\int_0^w e^{ib(\lambda n+\mu y)}ds\{1+e^{ib\mu y_1}+\&c.\}$$

The total integral will then be

$$\frac{\sin n\frac{ba\mu}{2}}{\sin\frac{ba\mu}{2}}\left[\frac{1-e^{ib\mu w}}{ib\mu}+\int_0^w e^{ib(\lambda x+\mu y)}ds\right]\left[1+e^{ib\mu y_1}+e^{ib\mu y_2}+\&c.\right].$$

As before, multiply this by the same with the sign of i changed to get the intensity.

Example 1.—Equal Distances.

The space a contains $n'-1$ equidistant grooves, so that $y_1=y_2-y_1=\&c.=\frac{a}{n'}$.

$$\Sigma_0^{n'-1}e^{ib\mu\frac{a}{n'}n}=e^{iba\mu}\frac{\sin\frac{ba\mu}{2}}{\sin\frac{ba\mu}{2n'}}.$$

Hence the displacement becomes

$$\frac{\sin n\frac{ba\mu}{2}}{\sin\frac{ba\mu}{2n'}}\left[\frac{1-e^{ib\mu w}}{ib\mu}+\int_0^w e^{ib(\lambda x+\mu y)}ds\right].$$

As the last term is simply the integral over the space $\frac{a}{n'}$ in a different form from before, this is a return to the form we previously had except that it is for a grating of nn' lines instead of n lines, the grating-space being $\frac{a}{n'}$.

Example 2.—Two Grooves.

$$1+e^{ib\mu y_1}=2e^{\frac{ib\mu y_1}{2}}\cos\frac{b\mu y_1}{2}.$$

But $ba\mu=2\mathrm{N}\pi$. Hence this becomes

$$2e^{i\pi\mathrm{N}\frac{y_1}{a}}\cos\pi\mathrm{N}\frac{y_1}{a}.$$

The square of the last term is a factor in the intensity. Hence the spectrum will vanish when we have

$$N\frac{y_1}{a} = \tfrac{1}{2},\ \tfrac{3}{2},\ \tfrac{5}{2},\ \&c.*$$

or

$$N = \frac{1}{2}\frac{a}{y_1}, \frac{3}{2}\frac{a}{y_1}, \frac{5}{2}\frac{a}{y_1}, \&c.$$

Thus when $\frac{a}{y_1} = 2$, the 1st, 3rd, &c., spectra will disappear, making a grating of twice the number of lines to the centim.

When $\frac{a}{y_1} = 4$, the 2nd, 6th, 10th, &c., spectra disappear.

When $\frac{a}{y_1} = 6$, the 3rd, 9th, &c., spectra disappear.

The case in which $\frac{a}{y_1} = 4$, as Lord Rayleigh has shown, would be very useful, as the second spectrum disappears leaving the red of the first and the ultra-violet of the third without contamination by the second. In this case two lines are ruled and two left out. This would be easy to do, but the advantages would hardly pay for the trouble owing to the following reasons:—Suppose the machine was ruling 20,000 lines to the inch. Leaving out two lines and ruling two would reduce the dispersion down to a grating with 5000 lines to the inch. Again, the above theory assumes that the grooves do not overlap. Now I believe that in nearly, if not all, gratings with 20,000 lines to the inch the whole surface is cut away and the grooves overlap. This would cause the second spectrum to appear again after all our trouble.

Let the grooves be nearly equidistant, one being slightly displaced. In this case $y_1 = \frac{a}{2} + v$.

$$\cos^2 \pi \frac{Ny_1}{2} = \left(\cos\frac{\pi N}{2}\cos\frac{\pi N v}{a} - \sin\frac{\pi N}{2}\sin\frac{\pi N v}{a}\right)^2.$$

For the even spectra this is very nearly unity, but for the odd it becomes

$$\left(\pi N \frac{v}{a}\right)^2.$$

Hence the grating has its principal spectra like a grating of space $\frac{a}{2}$; but there are still the intermediate spectra due to the space a, and of intensities depending on the *squares* of the order of spectrum, and the squares of the relative displace-

* A theorem of Lord Rayleigh's.

ment, a law which I shall show applies to the effect of all errors of the ruling.

This particular effect was brought to my attention by trying to use a tangent-screw on the head of my dividing-engine to rule a grating with, say, 28,872 lines to the inch, when a single tooth gave only 14,436 to the inch. However carefully I ground the tangent-screw I never was able to entirely eliminate the intermediate spectra due to 14,436 lines, and make a pure spectrum due to 28,872 lines to the inch, although I could nearly succeed.

Example 3.—One Groove in m misplaced.

Let the space a contain m grooves equidistant, except one which is displaced a distance v. The distance is now proportional to

$$1+e^{ib\mu\frac{a}{m}}+e^{2ib\mu\frac{a}{m}}+\&c.+e^{ib\mu\left(p\frac{a}{m}+v\right)}+\&c.+e^{ib\mu\frac{m-1}{m}a}$$

$$=e^{ib\mu\frac{m-1}{2m}a}\left\{\frac{\sin\frac{b\mu a}{2}}{\sin\frac{b\mu a}{2m}}+ib\mu v\,e^{ib\mu a\frac{2p-m+1}{2m}}\right\}.$$

Multiplying this by itself with $-i$ in place of $+i$, and adding the factors in the intensity, we have the whole expression for the intensity. One of the terms entering the expression will be

$$\frac{\sin n\frac{b\mu a}{2}}{\sin\frac{ba\mu}{2m}}\frac{\sin n\frac{ba\mu}{2}}{\sin\frac{ba\mu}{2}}\sin\frac{ba\mu}{2}\frac{2p-m+1}{m}.$$

Now the first two terms have finite values only around the points $\frac{ba\mu}{2}=m\mathrm{N}\pi$, where $m\mathrm{N}$ is a whole number. But $2p-m+1$ is also a whole number, and hence the last term is zero at these points. Hence the term vanishes and leaves the intensity, omitting the groove factor,

$$\frac{\sin^2 n\frac{ba\mu}{2}}{\sin\frac{ba\mu}{2m}}+(b\mu v)^2\frac{\sin^2 n\frac{ba\mu}{2}}{\sin^2\frac{ba\mu}{2}}.$$

The first term gives the principal spectra as due to a grating-space of $\frac{a}{m}$ and number of lines nm as if the grating were perfect. The last term gives entirely new spectra due to the grating-space a, and with lines of breadth due to a grating of n lines and intensities equal to $(b\mu v)^2$.

Hence, when the tangent-screw is used on my machine for 14,436 lines to the inch, there will still be present weak spectra due to the 14,436 spacing, although I should rule, say, 400 lines to the millim. This I have practically observed also.

The same law holds as before that the relative intensity in these subsidiary spectra varies as the square of the order of the spectrum and the square of the deviation of the line or lines from their true position.

So sensitive is a dividing-engine to periodic disturbances, that all the belts driving the machine must never revolve in periods containing an aliquot number of lines of the grating; otherwise they are sure to make spectra due to their period.

As a particular case of this section we have also to consider

Periodic Errors of Ruling.—Theory of "Ghosts."

In all dividing-engines the errors are apt to be periodic, due to "drunken" screws, eccentric heads, imperfect bearings, or other causes. We can then write

$$y = n_0 a + a_1 \sin(e_1 n) + a_2 \sin(e_2 n), + \&c.$$

The quantities e_1, e_2, &c. give the periods, and a_1, a_2, &c. the amplitudes of the errors. We can then divide the integral into two parts as before, an integral over the groove and spaces and a summation with respect to the numbers.

$$\Sigma \int_{y'}^{y''} e^{-ib(\lambda x + \mu y)} ds = \Sigma e^{-ib\mu y} \int_0^{y''-y'} e^{-ib(\lambda n + \mu y)} ds.$$

It is possible to perform these operations exactly; but it is less complicated to make an approximation, and take $y'' - y' = a$, a constant as it is very nearly in all gratings. Indeed the error introduced is vanishingly small. The integral which depends on the shape of the groove will then go outside the summation sign, and we have to perform the summation

$$\Sigma e^{-ib\mu \{a_0 n + a_1 \sin e_1 n + a_2 \sin e_2 n + \&c.\}}.$$

Let J_n be a Bessel's function. Then

$$\cos(u\sin\phi) = J_0(u) + 2[J_2(u)\cos_2\phi + J_4(u)\cos_4\phi + \&c.],$$

$$\sin(u\sin\phi) = \qquad 2[J_1(u)\sin\phi + J_3(u)\sin_3\phi + \&c.].$$

But

$$e^{-iu\sin\phi} = \cos(u\sin\phi) - i\sin(u\sin\phi).$$

Hence the summation becomes

$$\Sigma\left\{\begin{array}{l} e^{-ib\mu a_0 n} \\ \times[J_0(b\mu a_1) + 2(-iJ_1(b\mu a_1)\sin e_1 n + J_2(b\mu a_1)\cos 2e_1 n - \&c.) \\ \times[J_0(b\mu a_2) + 2(-iJ_1(b\mu a_2)\sin e_2 n + J_2(b\mu a_2)\cos 2e_1 n - \&c.) \\ \times[J_0(b\mu a_3) + \&c.)] \\ \times[\&c.]. \end{array}\right.$$

Case I.—Single Periodic Error.

In this case only a_0 and a_1 exist. We have the formula

$$\Sigma_0^{n-1} e^{-ipn} = e^{-i\frac{n-1}{2}p}\,\frac{\sin\frac{pn}{2}}{\sin\frac{p}{2}}.$$

Hence the expression for the intensity becomes

$$\left\{J_0(b\mu a_1)\frac{\sin n\frac{b\mu a_0}{2}}{\sin\frac{b\mu a_0}{2}}\right\}^2 + J_1^2(b\mu a_1)\left\{\left[\frac{\sin n\frac{b\mu a_0+e_1}{2}}{\sin\frac{b\mu a_0+e_1}{2}}\right]^2 + \left[\frac{\sin n\frac{b\mu a_0-e_1}{2}}{\sin\frac{b\mu a_0-e_1}{2}}\right]^2\right\} + \&c.$$

As n is large, this represents various very narrow spectral lines whose light does not overlap, and thus the different terms are independent of each other. Indeed, in obtaining this expression the products of quantities have been neglected for this reason because one or the other is zero at all points. These lines are all alike in relative distribution of light, and their intensities and positions are given by the following table :—

Places.	*Intensities.*	*Designations.*
$\mu = \frac{2\pi N}{ba_0}$.	$J_0^2(b\mu a_1)$.	Primary lines.
$\mu_1 = \mu \pm \frac{e_1}{ba_0}$.	$J_1^2(b\mu_1 a_1)$.	Ghosts of 1st order.
$\mu_2 = \mu \pm \frac{2e_1}{ba_0}$.	$J_2^2(b\mu_1 a_2)$.	Ghosts of 2nd order.
$\mu_3 = \mu \pm \frac{3e_1}{ba_0}$.	$J_3^2(b\mu_1 a_3)$.	Ghosts of 3rd order.
&c.	&c.	&c.

Hence the light which would have gone into the primary line now goes to making the ghosts, so that the total light in the line and its ghosts is the same as in the original without ghosts.

The relative intensities of the ghosts as compared with the primary line is

$$\frac{J_n^2(b\mu a_1)}{J_0^2(b\mu a_1)}.$$

This for very weak ghosts of the first, second, third, &c. order becomes

$$\left(\pi N \frac{a_1}{a_0}\right)^2, \quad \frac{1}{2}\left(\pi N \frac{a_1}{a_0}\right)^4, \quad \frac{1}{6}\left(\pi N \frac{a_1}{a_0}\right)^6, \text{ \&c.}$$

The intensity of the ghosts of the first order varies as the square of the order of the spectrum and as the square of the relative displacement as compared with the grating-space a_0. This is the same law as we before found for other errors of ruling; and it is easy to prove that it is general. Hence

The effect of small errors of ruling is to produce diffused light around the spectral lines. This diffused light is subtracted from the light of the primary line, and its comparative amount varies as the square of the relative error of ruling and the square of the order of the spectrum.

Thus the effect of the periodic error is to diminish the intensity of the ordinary spectral lines (primary lines) from the intensity I to $J_0^2(b\mu a_1)$, and surround it with a symmetrical system of lines called ghosts, whose intensities are given above.

When the ghosts are very near the primary line, as they nearly always are in ordinary gratings ruled on a dividing-

engine with a large number of teeth in the head of the screw, we shall have

$$J_1^2 ba_1\left(\mu+\frac{e_1}{ba_0}\right)+J_1^2 ba_1\left(\mu-\frac{e_1}{ba_0}\right)=2J_1^2 ba_1\mu \text{ nearly.}$$

Hence the total light is by a known theorem,

$$J_0^2+2[J_1^2+J_2^2+\&c.]=1.$$

Thus, in all gratings, the intensity of the ghosts as well as the diffused light increases rapidly with the order of the spectrum. This is often marked in gratings showing too much crystalline structure. For the ruling brings out the structure and causes local difference of ruling which is equivalent to error of ruling as far as diffused light is concerned.

For these reasons it is best to get defining power by using broad gratings and a low order of spectra, although the increased perfection of the smaller gratings makes up for this effect in some respects.

There is seldom advantage in making both the angle of incidence and diffraction more than 45°, but if the angle of incidence is 0, the other angle may be 60°, or even 70°, as in concave gratings. Both theory and practice agree in these statements.

Ghosts are particularly objectionable in photographic plates, especially when they are exposed very long. In this case ghosts may be brought out which would be scarcely visible to the eye.

As a special case, take the following numerical results :—

N	$=$	1.			2.			3.	
$\frac{a_1}{a_0}$	$=$	$\frac{1}{25}$,	$\frac{1}{50}$,	$\frac{1}{100}$.	$\frac{1}{25}$,	$\frac{1}{50}$,	$\frac{1}{100}$.	$\frac{1}{25}$,	$\frac{1}{50}$, $\frac{1}{100}$.
$\left(\pi N\frac{a_1}{a_0}\right)^2$	$=$	$\frac{1}{63}$,	$\frac{1}{252}$,	$\frac{1}{1008}$.	$\frac{1}{16}$,	$\frac{1}{63}$,	$\frac{1}{252}$.	$\frac{1}{7}$,	$\frac{1}{28}$, $\frac{1}{102}$.

In a grating with 20,000 lines to the inch, using the third spectrum, we may suppose that the ghosts corresponding to $\frac{a_1}{a_0}=\frac{1}{50}$ will be visible and those for $\frac{a_1}{a_0}=\frac{1}{25}$ very trouble-

some. The first error is $a_1 = \frac{1}{1000000}$ in. and the second $a_1 = \frac{1}{500000}$ in. Hence a periodic displacement of one millionth of an inch will produce visible ghosts and one five-hundredth-thousandth of an inch will produce ghosts which are seen in the second spectrum and are troublesome in the third. With very bright spectra these might even be seen in the first spectrum. Indeed an over-exposed photographic plate would readily bring them out.

When the error is very great, the primary line may be very faint or disappear altogether, the ghosts to the number of twenty or fifty or more being often more prominent than the original line. Thus, when

$$b\mu a_1 = 2{\cdot}405,\ 5{\cdot}52,\ 8{\cdot}65,\ \&c. = 2\pi N\frac{a_1}{a_0},$$

the primary line disappears. When

$$b\mu a_1 = 0,\ 3{\cdot}83,\ 7{\cdot}02,\ \&c. = 2\pi N\frac{a_1}{a_0},$$

the ghosts of the first order will disappear. Indeed, we can make any ghosts disappear by the proper amount of error.

Of course, in general

$$J_n = \frac{2(n-1)}{v} J_{n-1} - J_{n-2}.$$

Thus a table of ghosts can be formed readily and we can always tell when the calculation is complete by taking the sum of the light and finding unity (see p. 414).

This table shows how the primary line weakens and the ghosts strengthen as the periodic error increases, becoming 0 at $2\pi N\frac{a_1}{a_0} = 2{\cdot}405$. It then strengthens and weakens periodically, the greatest strength being transferred to one of the ghosts of higher and higher order as the error increases.

Thus one may obtain an estimate of the error from the appearance of the ghost.

Some of these wonderful effects with 20 to 50 ghosts stronger than the primary line I have actually observed in a grating ruled on one of my machines before the bearing end of the screw had been smoothed. The effect was very similar to these calculated results.

$2\pi N\frac{a_1}{a_0}$.	J_0^2.	J_1^2.	J_2^2.	J_3^2.	J_4^2.	J_5^2.	J_6^2.	J_7^2.	J_8^2.	J_9^2.	J_{10}^2.	J_{11}^2.	J_{12}^2	J_{13}^2.	J_{14}^2.
0·0 ...	1·000	...	...	...	...	...	...	...	...	...	...	...	...	...	...
·2 ...	·980	·010	...	...	...	...	...	...	...	...	...	...	...	...	...
·4 ...	·922	·038	...	...	...	...	...	...	...	...	...	...	...	...	...
·6 ...	·832	·082	·002	...	...	...	...	...	...	...	...	...	...	...	...
·8 ...	·716	·136	·005	...	...	...	...	...	...	...	...	...	...	...	...
1·0 ...	·586	·194	·012	...	...	...	...	...	...	...	...	...	...	...	...
2·0 ...	·050	·333	·124	·017	·001	...	...	...	...	...	...	...	...	...	...
2·605 ...	·000	·269	·186	·040	·003	...	...	...	...	...	...	...	...	...	...
3·0 ...	·068	·115	·236	·095	·017	·002	...	...	...	...	...	...	...	...	...
3·832 ..	·162	·000	·162	·176	·065	·013	·002	...	...	...	...	...	...	...	...
4·0 ...	·158	·004	·133	·185	·079	·018	·002	...	...	...	...	...	...	...	...
5·0 ...	·031	·107	·002	·133	·153	·068	·017	·003	...	...	...	...	...	...	...
5·520 ...	·000	·116	&c.												
6·0 ...	·022	·077	·059	·013	·128	·131	·061	·017	·003	...	...	...	...	...	...
7·016 ...	·090	·000	·090	&c.											
8·0 ...	·029	·055	·013	·085	·011	·035	·114	·103	·050	·016	·003	·001	...	...	...
8·654 ...	·000	·075	&c.												
10·0 ...	·060	·002	·065	·003	·048	·055	·002	·047	·101	·091	·051	·022	·011	·009	·022

Double Periodic Error.

Supposing as before that there is no overlapping of the lines, we have the following :—

Places.	*Intensities.*	
$\mu = \frac{2\pi N}{ba_0}$.	$[J_0(b_1 a\mu)\ J_0(ba_2\mu)]^2$.	Primary order.
$\mu_1 = \mu \pm \frac{e_1}{ba_0}$.	$[J_1(ba_1\mu_1)\ J_0(ba_2\mu_1)]^2$.	Ghosts of 1st order.
$\mu_2 = \mu \pm \frac{e_2}{ba_0}$.	$[J_0(ba_1\mu_2)\ J_1(ba_2\mu_2)]^2$.	
$\mu_3 = \mu \pm \frac{e_1 \pm e_2}{ba_0}$.	$[J_1(ba_1\mu_3)\ J_1(ba_2\mu_3)]^2$.	Ghosts of 2nd order.
$\mu_4 = \mu \pm \frac{2e_1}{ba_0}$.	$[J_2(ba_1\mu_4)\ J_0(ba_2\mu_4)]^2$.	
$\mu_5 = \mu \pm \frac{2e_2}{ba_0}$.	$[J_0(ba_1\mu_5)\ J_2(ba_2\mu_5)]^2$.	
$\mu_6 = \mu \pm \frac{e_1 \pm 2e_2}{ba_0}$.	$[J_1(ba_1\mu_6)\ J_2(ba_2\mu_6)]^2$.	Ghosts of 3rd order.
$\mu_7 = \mu \pm \frac{2e_1 \pm e_2}{ba_0}$.	$[J_2(ba_1\mu_7)\ J_1(ba_2\mu_7)]^2$.	
$\mu_8 = \mu \pm \frac{3e_1}{ba_0}$.	$[J_0(ba_1\mu_8)\ J_3(ba_2\mu_8)]^2$.	
$\mu_9 = \mu \pm \frac{3e_2}{ba_0}$.	$[J_3(ba_2\mu_9)\ J_0(ba_2\mu_9)]^2$.	
&c.	&c.	

Each term in this table of ghosts simply expresses the fact that each periodic error produces the same ghosts in the same place as if it were the only error, while others are added which are the ghosts of ghosts. The intensities, however, are modified in the presence of these others.

Writing $c_1 = ba_1\mu$ and $c_2 = ba\mu_2$.

The total light is

$$J_0^2(c_1)\ J_0^2(c_2) + \left\{ \begin{array}{r} 2J_1^2(c_1)\ J_0^2(c_2) \\ +2J_0^2(c_1)\ J_1^2(c_2) \end{array} \right\} + \left\{ \begin{array}{r} 2J_2^2(c_1)\ J_0^2(c_2) \\ +4J_1^2(c_1)\ J_1^2(c_2) \\ +2J_0^2(c_1)\ J_2^2(c_2) \end{array} \right\} + \&c$$

which we can prove to be equal to 1.

Hence the sum of all the light is still unity, a general proposition which applies to any number of errors.

The positions of the lines when there is any number of periodic errors can always be found by calculating first the ghosts due to each error separately; then the ghosts due to these primary ghosts for it as if it were the primary line, and so on *ad infinitum*.

In case the ghosts fall on top of each other the expression for the intensity fails. Thus when $e_2=2e_1$, $e_3=3e_1$, &c., the formula will need modification. The positions are in this case only those due to a single periodic error, but the intensities are very different.

Places.	
$\mu = \frac{2\pi N}{ba_0}$.	$[J_0(ba_1\mu)J_0(ba_2\mu)]^2$.
$\mu_1 = \mu \pm \frac{e_1}{ba_0}$.	$\left\{ \begin{array}{l} [J_1(ba_1\mu_1)J_0(ba_2\mu_1) - J_3(ba_1\mu_1)J_2(ba_2\mu_1) + \&c.]^2 \\ + [J_1(ba_1\mu_1)J_1(ba_2\mu_1) - J_3(ba_1\mu_1)J_1(ba_2\mu_1) + \&c.]^2. \end{array} \right.$
&c.	&c.

We have hitherto considered cases in which the error could not be corrected by any change of focus in the objective. It is to be noted, however, that for any given angle and focus every error of ruling can be neutralized by a proper error of the surface, and that all the results we have hitherto obtained for errors of ruling can be produced by errors of surface, and many of them by errors in size of groove cut by the diamond. Thus ghosts are produced not only by periodic errors of ruling but by periodic waves in the surface, or even by a periodic variation in the depth of ruling. In general, however, a given solution will apply only to one angle and, consequently, the several results will not be identical; in some cases, however, they are perfectly so.

Let us now take up some cases in which change of focus can occur. The term κr^2 in the original formula must now be retained.

Let the lines of the grating be parallel to each other. We can then neglect the terms in z and can write $r^2=y^2$ very nearly. Hence the general expression becomes

$$\int e^{ib(\lambda x+\mu y-\kappa y^2)}ds,$$

where κ depends on the focal length. This is supposed to be very large, and hence κ is small.

The integral can be divided into two parts—an integral over the groove and the intervening space, and a summation for all the grooves. The first integral will slightly vary with

change in the distance of the grooves apart, but this effect is vanishingly small compared with the effect on the summation, and can thus be neglected. The displacement is thus proportional to

$$\Sigma e^{ib(\mu y-\kappa y^2)}.$$

Case I.—Lines at Variable Distances.

In this case we can write in general

$$y=an+a_1n^2+a_2n^3+\&c.$$

As κ, a_1, a_2, &c., are small, we have for the displacement, neglecting the products of small quantities,

$$\Sigma e^{ib[\mu(an+a_1n^2+a_2n^3+\&c.)-\kappa a^2n^2]}.$$

Hence the term a_1n^2 can be neutralized by a change of forms expressed by $\mu a_1=\kappa a^2$. Thus a grating having such an error will have a different focus according to the angle n, and the change will be + on one side and − on the other.

This error often appears in gratings and, in fact, few are without it.

A similar error is produced by the plate being concave, but it can be distinguished from the above error by its having the focus at the same angle on the two sides the same instead of different.

According to this error, a_1n^2, the spaces between the lines from one side to the other of the grating, increase uniformly in the same manner as the lines in the B group of the solar spectrum are distributed. Fortunately it is the easiest error to make in ruling, and produces the least damage.

The expression to be summed can be put in the form

$$\Sigma e^{ib\mu an}[1+ib(\mu a_1-\kappa a^2)n^2+ib\mu a_2n^3+ib[\mu a_3+ib(\mu a_1-\kappa a^2)^2]n^4 \\ +\&c.]$$

The summation of the different terms can be obtained as shown below, but, in general, the best result is usually sought by changing the focus. This amounts to the same as varying κ until $\mu a_1-\kappa a^2=0$ as before. For the summation we can obtain the following formula from the one already given. Thus

$$\Sigma_0^{n-1} e^{2ipn}=\frac{\sin np}{\sin p}e^{ip(n-1)}.$$

Hence

$$\Sigma_0^{n-1} n^m e^{2ipn}=\frac{1}{(2i)^m}e^{ip(n-1)}\left(\frac{d}{dp}+i(n-1)\right)^m\frac{\sin np}{\sin p}.$$

When n is very large, writing $\frac{b\mu an}{2}=pn=\pi Nn+q$, we have

$$\Sigma_0^{n-1} n^m e^{2ipn} = \frac{n^{m+1}}{(2i)^m} e^{iq}\left(\frac{d}{dq}+i\right)^m \frac{\sin q}{q}.$$

Whence, writing

$$\begin{aligned} c &= b(\mu a_1-\kappa a^2), \\ c' &= b\mu a_2, \\ c'' &= b[\mu a_3+ib(\mu a_1-\kappa a^2)^2], \\ c''' &= \&c., \end{aligned}$$

the summation is

$$e^{iq}\left\{\begin{aligned} & n+i\left(c\frac{n^3}{4}+c'\frac{n^4}{8}+c''\frac{n^5}{16}+\right) \\ & +\left(2c\frac{n^3}{4}+3c'\frac{n^4}{8}+4c''\frac{n^5}{16}+\right)\frac{d}{dq} \\ & -i\left(c\frac{n^3}{4}+3c'\frac{n^4}{8}+6c''\frac{n^5}{16}+\right)\frac{d^2}{dq^2} \\ & -\left(c'\frac{n^4}{8}+4c''\frac{n^5}{16}+\right)\frac{d^3}{dq^3} \\ & +i\left(c''\frac{n^5}{16}+\right)\frac{d^4}{dq^4} \\ & +\&c. \end{aligned}\right\}\frac{\sin q}{q},$$

$$\frac{d}{dq}\frac{\sin q}{q}=\frac{q\cos q-\sin q}{q^2},$$

$$\frac{d^2}{dq^2}\frac{\sin q}{q}=\frac{-2q\cos q+(2-q^2)\sin q}{q^3},$$

$$\frac{d^3}{dq^3}\frac{\sin q}{q}=\frac{q(6-q^2)\cos q-(6-3q^2)\sin q}{q^4},$$

&c. &c.

These equations serve to calculate the distribution of light intensity in a grating with any error of line distribution suitable to this method of expansion and at any focal length. For this purpose the above summation must be multiplied by itself with $+i$ in place of $-i$.

The result is for the light intensity

$$\left\{ n\frac{\sin q}{q} + \left(2c\frac{n^3}{4} + 2c\frac{n^4}{8} + \&c.\right)\frac{d}{dq}\frac{\sin q}{q} - \left(c'\frac{n^4}{8} + 4c''\frac{n^5}{16} + \&c.\right)\frac{d^3}{dq^3}\frac{\sin q}{q} + \&c. \right\}^2$$

$$+ \left\{ \left(c\frac{n^3}{4} + 3c'\frac{n^4}{8} + \&c.\right)\frac{d^2}{dq^2}\frac{\sin q}{q} - \left(c''\frac{n^5}{16} + \&c.\right)\frac{d^4}{dq^4}\frac{\sin q}{q} + \&c. \right\}^2.$$

As might have been anticipated, the effect of the additional terms is to broaden out the line and convert it into a rather complicated group of lines, as can sometimes be observed with a bad grating. At any given angle the same effect can be produced by variation of the plate from a perfect plane. Likewise the effect of errors in the ruling may be neutralized for a given angle by errors of the ruled surface, as noted in the earlier portions of the paper.

XL. *On the Differential Equation of Electrical Flow.* *By* T. H. Blakesley, *M.A.**

THE object of this paper is to point out that the theory of electrical discharge, as exemplified in the mathematical expressions employed to represent the physical facts, is incompetent to explain all the phenomena observed in extreme cases; and to show that the admission of certain properties of matter not usually recognized is the only way of satisfactorily obviating the imperfection of the existing views.

In some of the investigations I shall not employ exclusively algebraical symbolic methods, but, where it may more advantageously be adopted, I shall avail myself of the geometrical method. Such cases most frequently arise where magnitudes under consideration are capable of having negative values. All tidal effects, using the word in its most general sense, involve such magnitudes.

Electrical currents in a given conductor may have all possible values in one direction or in the opposite direction, but are otherwise restricted.

The projection of the line joining two points in space upon a fixed straight line is a geometrical magnitude of this sort. With respect to the direction in space, sometimes one of the projected points will be on one side of the other

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projected point, sometimes on the other. So that such a line has all the properties necessary for representing another magnitude of the same character.

In this way I shall most generally make the projection represent Electromotive Force, but occasionally Field of Magnetism at a point. As to matter of nomenclature, the only scientific term which I shall employ admitting of any doubtful interpretation, is the Effective Electromotive Force. By this term I intend to convey the idea of that electromotive force which is numerically equal to the product of the current and the resistance, at a point of time. As a department of State has recently employed the term in a totally different sense, this statement has appeared to me to be necessary in the interests of proper explanation. The effective electromotive force is the algebraical sum of all the impressed and induced electromotive forces, and is here represented by E. If V is the sum of all the impressed electromotive forces and F is the sum of all induced electromotive forces, then the equation among their quantities is $V+F=E$ universally.

Geometrically, if A B, B C are lines whose projections on some one fixed straight line represent the sum of the impressed and the sum of the induced electromotive forces respectively, then the projection of A C will represent the effective electromotive force.

The three lines must form the sides of a triangle, those corresponding to the impressed and induced electromotive forces being taken the same way round the triangle, that corresponding to E being taken in the opposite direction.

Now if the actual changes in the magnitudes are harmonic, and of the same period, it is clear that the lines A B, B C, A C must remain of constant length and the triangle must rotate in its own plane at a uniform rate of such a value as to perform a complete revolution in the period of the harmonic change. The triangle thus shows admirably the way in which these magnitudes succeed one another in phase. It also follows from the properties of harmonic motion that if two magnitudes have the same harmonic period, but differ in phases by a quarter of the whole period, the corresponding lines to be projected are at right angles with each other. And hence the rate of variation of an harmonic magnitude differs in phase from the magnitude itself by a quarter of the period. But in the simplest case of a circuit being plied with an harmonic electromotive force V, it is generally considered that the induced electromotive force varies as the

rate of change of the current; that is

$$F = -L\frac{dC}{dt} = -\frac{L}{R}\frac{dE}{dt}, \text{ for } E = RC,$$

where C is the current, R the resistance, and L is the coefficient of self-induction.

The equation already given then becomes

$$V - L\frac{dC}{dt} = E = RC.$$

Multiplying through by C and integrating through a complete period,

$$\int VC\,dt - L\int C\frac{dC}{dt}\,dt = R\int C^2 dt.$$

The first term represents the work done by the source of the disturbance.

The second term vanishes.

The third term represents work done in heating the circuit.

Hence the whole work done has gone to heat the circuit.

Now it is admitted on all hands that when the period is sufficiently short a radiation of energy into space takes place. A portion of this radiated energy is sometimes caught by means of a neighbouring circuit and converted into heat.

A coefficient of mutual induction and a corresponding extra term is then introduced into the equation. But are we to suppose that radiation would not proceed into space were there no neighbouring conductor? It is against probability, against the electromagnetic theory of light.

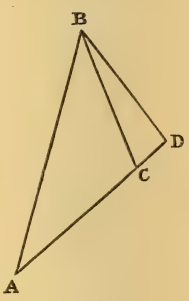
If electromagnetic waves are capable of being sent into space, we can no longer look upon the operation of establishing a current in a circuit as analogous to bending a stiff spring or displacing rigid wheelwork. The wheelwork must have indiarubber spokes or teeth.

The above equation takes no account of this radiation which is expended outside the wire, nor of any other work done elsewhere than in the conductor; and this latter the equation states to be exactly equal to the energy expended in propagating the electromotive force. Even supposing a portion of the field is occupied by some material whose passage through a cycle of magnetization involves the loss of energy, in the form of heat, this, equally with wave-propagation through space occupied by perfectly elastic matter, will not be accounted for by the equation.

Now of such phenomena as radiation of energy in electromagnetic waves, or absorption of energy in the field, there is

ample evidence. Therefore an equation will not meet such cases in which the induced electromotive force is taken as entirely in quadrature with the current, or when F is wholly of the form $-L\frac{dC}{dt}$.

Hence, in the geometrical representation it is clear that the induced electromotive-force line must not be exactly at right angles with that of the effective electromotive-force line; *i. e.* the angle B C A is not exactly a right angle; and it is easy to see that it must be greater than a right angle, for B C may be resolved into B D . D C, where B D C is a right angle and A C D is one straight line. For then the whole work done is equal to $\frac{AD.AC}{2R}$. The work done in heating the conductor is $\frac{AC.AC}{2R}$, and the difference, or the work done in the field, is $\frac{AC.DC}{2R}$.



Hence, if D lies on the side of C nearer to A, A D would be less than A C, and the work done by the discharge would be less than that required to heat the conductor: in other words, energy would have to be received from space.

Hence the induced electromotive forces may be represented by two components—one A D in quadrature with the current, and one D C in opposition to it,

$$-L\frac{dC}{dt}-\lambda C,$$

where λ may or may not be a constant, but is in kind a resistance.

The equation among the electromotive forces may be written

$$V-L\frac{dC}{dt}-\lambda C=RC.$$

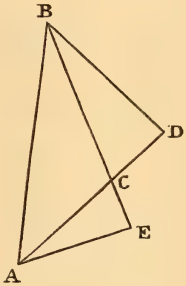
Multiplying through by Cdt and integrating through a complete period,

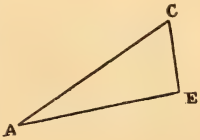
$$\int VCdt-L\int C\frac{dC}{dt}dt=R\int C^2dt+\int\lambda C^2dt.$$

The second term on the left vanishes as before, the first term representing the whole work done. On the right the

first term heats the conductor and the second term gives energy to space.

We may go somewhat further into the causes of such an induced electromotive-force component if we employ the geometrical mode of symbolizing the electric quantities. BC, the induced electromotive-force line, should be at right angles to the induction through the circuit, for it is the rate of increase of the latter which produces the former. Hence if A E is a perpendicular let fall upon B C produced, A E will represent the phase of the magnetic induction. But A C being in phase with the current is in phase with the field. Hence E A C, or C B D which is equal to it, is a magnetic phase-lag, and A E may be said to be in phase with the *effective* field, and therefore with the induction. This suggests that if we employ the lower lines of the figure to represent *fields*, we may make up a triangle A C E such that A C is the impressed field, C E an induced field, and A E an effective field, of course when, as usual, projected on a fixed line; C E being perhaps, though by no means certainly, at right angles to A E. However, whether C E here has in any case two components perpendicular and parallel respectively to A E or not, it appears very certain that the perpendicular component must exist. Assuming at first that it alone exists,—





If we employ small letters :—

v for impressed field $=$ AC,
f for induced field $=$ CE,
e for effective field $=$ AE,
l = coefficient of magnetic self-induction, so that

$$f = -l\frac{dI}{dt};$$

and μ for the permeability, I for the rate of magnetic induction, *i. e.* per square centim., we have

$$v - l\frac{dI}{dt} = e = \frac{I}{\mu}.$$

To obtain an equation of energy from this we must multiply (not by I, as analogy would at first sight perhaps dictate) by $\frac{dI}{dt} \cdot dt \times$ cross section, for the formula for energy is

$$[l^2t^{-2}m] \equiv [\mu^{-\frac{1}{2}}l^{-\frac{1}{2}}t^{-1}m^{\frac{1}{2}}][\mu^{\frac{1}{2}}l^{\frac{1}{2}}t^{-2}m^{\frac{1}{2}}]t$$

$$\equiv \left[\text{Field}\right]\left[\frac{\text{lines}}{t}\right]t$$

$$\int v\frac{dI}{dt}.dt - l\int\left(\frac{dI}{dt}\right)^2 dt = \int\frac{I}{\mu}\frac{dI}{dt}.dt.$$

Here the term on the right hand disappears necessarily, and the work expended, if any, is equal to $l\int\left(\frac{dI}{dt}\right)^2 dt$. Hence this work vanishes only if $l=0$, *i. e.*, if there is no component field in quadrature with the induction ; a curious antithesis to the electric problem. If there were a field induced in phase with the induction, it would not result in the dissipation of energy. No argument for such a state of things can be drawn on the score of loss of energy.

If the phases of magnetism in any cycle coincided with the phases of field, there could be no such thing as hysteresis ; and, further, no radiation of energy from an alternating magnet.

But both these phenomena have been for many years recognized. It follows, therefore, that when induction through any space changes, a magnetic field is induced acting counter to the change.

Now it may be noticed that the tangents of the angles of lag, whether electric or magnetic, involve a coefficient in their numerator and the value of the period in their denominator. They therefore become larger as the period is made less. It might therefore happen that extreme rapidity of change would be necessary before a lag of current or of induction could be detected. Electric lags, or, at all events, the coefficients of self-induction can readily be measured. Magnetic lags have been measured by the author in certain cases by special artifices, but when we deal with a medium of small permeability, as air, the period must be extremely minute to make the lag-angle sensible, and as yet no machines possess a sufficient frequency to effect it. Recourse has been had to the rapid oscillations which take place when a Leyden jar is discharged. In these cases the radiation has been frequently caught and approximately measured, and it is therefore in these very cases that the rectification of the formula becomes important.

I propose to investigate by geometry and otherwise the conditions under which a Leyden jar is discharged. Geometry especially will afford an excellent and graphic insight into the question of the oscillatory discharge.

As in the case of the sustained discharge, I shall first take the usual formula, obtain the geometrical illustration of it, and, observing where the defect shows itself, pass by an easy transition to the truer state of things.

In the case of the discharge of a condenser through a simple circuit removed from proximity with any other, we have the following equations to deal with :—

The general equation $V+F=E$, ... (i.)

$$E = RC, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

$$F = -L\frac{dC}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

$$C = -K\frac{dV}{dt}, \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

where

C is the current discharging the condenser ;
K is the capacity of the condenser ;
L is the coefficient of self-induction ;
R is the resistance ;
F is the induced electromotive force ;
E is the effective electromotive force ;
V is the potential difference of the plates of the condenser.

Eliminating E and F from (i.) by means of (ii.) and (iii.),

$$V-L\frac{dC}{dt}-RC=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

Differentiating,

$$\frac{dV}{dt}-L\frac{d^2C}{dt^2}-R\frac{dC}{dt}=0,$$

and substituting for $\frac{dV}{dt}$ from (iv.),

$$-\frac{C}{K}-L\frac{d^2C}{dt^2}-R\frac{dC}{dt}=0,$$

or

$$C+KR\frac{dC}{dt}+LK\frac{d^2C}{dt^2}=0,$$

the differential equation of C.

Since $C=\frac{E}{R}$, it follows that the equation

$$E+KR\frac{dE}{dt}+LK\frac{d^2E}{dt^2}=0$$

is also true, and therefore is the differential equation of E.

Again, from (v.) and (iv.), since $\frac{dC}{dt} = -K\frac{d^2V}{dt^2}$, obtained by differentiating (iv.),

$$V + RK\frac{dV}{dt} + LK\frac{d^2V}{dt^2} = 0.$$

This is the differential equation of V.

Thirdly, differentiating twice the equation

$$V + F - RC = 0,$$

$$\frac{d^2V}{dt^2} + \frac{d^2F}{dt^2} - R\frac{d^2C}{dt^2} = 0,$$

from (iii.) by differentiation it is seen that

$$\frac{d^2C}{dt^2} = -\frac{1}{L}\frac{dF}{dt},$$

and from (iv.),

$$\frac{d^2V}{dt^2} = -\frac{1}{K}\frac{dC}{dt},$$

which is further reduced to $\frac{1}{K}\frac{F}{L}$ by (iii.).

Hence
$$\frac{F}{KL} + \frac{d^2F}{dt^2} + \frac{R}{L}\frac{dF}{dt} = 0,$$

or

$$F + KR\frac{dF}{dt} + KL\frac{d^2F}{dt^2} = 0,$$

the differential equation of F.

It is thus clear that the variables V, F, E, C, all have the same form of differential equation, viz.:—

$$E + KR\frac{dE}{dt} + KL\frac{d^2E}{dt^2} = 0.$$

Of course, to make this equation homogeneous,

KR is of the order (time) ;
KL „ „ (time)^2.

KL may be written $KR \cdot \frac{L}{R}$, or still better $\frac{KR}{2} \cdot \frac{2L}{R}$.

If we write
$$\frac{2L}{R} = t_1$$

and
$$\frac{KR}{2} = t_3,$$

t_1 and t_3 are time-constants of the circuit, and the differential

equation may be written

$$E + 2t_3 \frac{dE}{dt} + t_1 t_3 \frac{d^2E}{dt^2} = 0.$$

In this expression the two time-constants may be considered to be independent.

To obtain a geometrical representation of the changes :—

(1) Suppose a line, whose length is r, to shrink logarithmically so that its change is represented by the equation

$$\frac{dr}{dt} = -\frac{r}{t_1},$$

where t_1 is a time-constant.

Then

$$r = ae^{-\frac{t}{t_1}},$$

where a is the value of r at the beginning of the time, and t_1 appears as the time taken for r to shrink to $\frac{1}{e}$ of itself.

(2) Secondly, suppose a straight line in a plane to constantly change in *direction* at a uniform rate, in the same sense. If θ is the angle measured from a fixed direction,

$$\frac{d\theta}{dt} = \frac{2\pi}{t_2},$$

where t_2 is a time-constant. Hence

$$\theta = \frac{2\pi}{t_2} . t.$$

Whence t_2 appears as the time required to describe 2π.

(3) Suppose a line to undergo both the changes contemplated, which is possible, since one is a change of length, the other a change in direction. Then, eliminating the time, we have

$$r = ae^{-\frac{\theta}{\frac{2\pi t_1}{t}}},$$

or $r = ae^{-\frac{\theta}{\tan\beta}}$, where $\tan\beta = \frac{2\pi t_1}{t_2}$.

This is the equation of the equiangular spiral, with the characteristic angle β, whose value merely depends upon the two time-constants t_1 and t_2.

(4) Now imagine this length r constantly projected on some fixed straight line, and for simplicity take this straight line as at right angles to the direction in which $\theta = 0$.

Then the projection under consideration (E) has for its expression

$$E = a . e^{-\frac{\theta}{\tan\beta}} \sin\theta ;$$

i. e., it consists of a constant factor, a logarithmical factor, and a rhythmical or harmonic factor.

Substituting for θ its value $\frac{2\pi}{t_2} \cdot t$,

$$E = a \cdot e^{-\frac{2\pi}{t \tan\beta} \cdot t} \sin \frac{2\pi}{t_2} \cdot t,$$

$$E = a e^{-\frac{\theta}{\tan\beta}} \sin\theta,$$

$$\frac{dE}{d\theta} = a e^{-\frac{\theta}{\tan\beta}} \cos\theta - \frac{a}{\tan\beta} e^{-\frac{\theta}{\tan\beta}} \sin\theta$$

$$= a e^{-\frac{\theta}{\tan\beta}} \cos\theta - \frac{E}{\tan\beta}.$$

$$\frac{d^2E}{d\theta^2} = -\frac{1}{\tan\beta}\frac{dE}{d\theta} - a e^{-\frac{\theta}{\tan\beta}} \sin\theta - \frac{a}{\tan\beta} e^{-\frac{\theta}{\tan\beta}} \cos\theta$$

$$= -\frac{1}{\tan\beta}\frac{dE}{d\theta} - E - \frac{1}{\tan\beta}\left\{\frac{dE}{d\theta} + \frac{E}{\tan\beta}\right\}$$

$$= -\frac{2}{\tan\beta}\frac{dE}{d\theta} - E\left\{1 + \frac{1}{\tan^2\beta}\right\};$$

therefore

$$E + \frac{2\tan\beta}{1+\tan^2\beta}\frac{dE}{d\theta} + \frac{\tan^2\beta}{1+\tan^2\beta}\frac{d^2E}{d\theta^2} = 0.$$

Now

$$\frac{dE}{d\theta} = \frac{dE}{dt} \cdot \frac{dt}{d\theta} = \frac{dE}{dt} \cdot \frac{t_2}{2\pi},$$

therefore

$$\frac{d^2E}{d\theta^2} = \frac{d^2E}{dt^2} \cdot \frac{dt}{d\theta}\frac{t_2}{2\pi} = \frac{d^2E}{dt^2}\left(\frac{t_2}{2\pi}\right)^2,$$

therefore

$$E + \frac{2\tan\beta}{1+\tan^2\beta}\frac{t_2}{2\pi} \cdot \frac{dE}{dt} + \frac{\tan^2\beta}{1+\tan^2\beta}\left(\frac{t_2}{2\pi}\right)^2 \frac{d^2E}{dt^2} = 0;$$

which, since $\tan\beta = \frac{2\pi t_1}{t_2}$, becomes

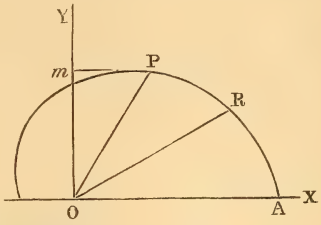
$$E + \frac{2t_1}{(1+\tan^2\beta)}\frac{dE}{dt} + \frac{t_1^2}{(1+\tan^2\beta)}\frac{d^2E}{dt^2} = 0;$$

and if t_3 is written for $\frac{t_1}{(1+\tan^2\beta)}$,

$$E + 2t_3\frac{dE}{dt} + t_1 t_3 \frac{d^2E}{dt^2} = 0.$$

An equation which is at once comparable with those obtained in the Electrical problem.

It thus appears that the variables in the problem of electrical discharge under consideration may be represented by the projections of three sides of a triangle, which is constantly undergoing uniform rotation and linear logarithmic shrinking. Let the figure represent a portion of the appropriate curve whose characteristic angle is β, and let O R be some radius vector. Then the projection of O R on O Y will be a maximum when the tangent at R is parallel to O X. Let P be such a position, and let P M be the tangent at P. Then M P O = P O X = β.

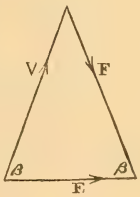


Now suppose O A the line representing (in its projection) the effective electromotive force about to change sign through the value zero. This means that the current is about to change sign, and the condenser having been receiving current is about to begin to be discharged, *i. e.* its charge and therefore potential difference is a maximum. Then the line of P.D. must make the angle P O A with the line of *effective E.M.F.*

Again, the E.M.F. of self-induction is zero when the current is at a maximum, by the nature of the ordinary hypothesis.

Therefore, when the line representing E makes an angle β with O X, the line representing induced E.M.F. (F) must be parallel with it. Hence it also makes an angle β with the line of effective E.M.F.; but in phase lags behind it, whereas the P.D. is in advance by that angle.

Thus, if on any line taken as base we construct an *isosceles* triangle of appropriate base angles, the sides will represent the P.D. of the condenser and the induced E.M.F. of self-induction respectively, and the base will represent the effective E.M.F. It only remains to rotate the triangle with appropriate speed and to allow it to shrink at the due logarithmic rate.



The properties of the triangle agree exactly with the electrical properties.

The angle β is such that $\tan\beta = \frac{2\pi t_1}{t_2}$;

therefore $$\cos^2\beta = \frac{1}{1+\left(\frac{2\pi t_1}{t_2}\right)^2} = \frac{t_3}{t_1} = \frac{\frac{\mathrm{KR}}{2}}{\frac{2\mathrm{L}}{\mathrm{R}}} = \frac{\mathrm{KR}^2}{4\mathrm{L}};$$

therefore $\cos\beta = \sqrt{\frac{K}{L}} \cdot \frac{R}{2}$, and β can have a real existence when $\frac{KR^2}{4L} < 1$;—the condition of Oscillatory Discharge.

The complete period is t_2, and is obtained in the electrical quantities thus ;—

$$\tan\beta = \frac{2\pi t_1}{t_2};$$

therefore

$$t_2^2 = \frac{(2\pi)^2 t_1^2}{\tan^2\beta} = \frac{(2\pi)^2 t_1^2}{\sec^2\beta - 1};$$

and $\cos^2\beta = \frac{t_3}{t_1}$ already obtained ;

therefore

$$t_2^2 = \frac{4\pi^2 t_3 t_1}{1 - \frac{t_3}{t_1}} = \frac{4\pi^2 KL}{1 - \left(\frac{KR^2}{4L}\right)};$$

therefore

$$t_2 = \frac{2\pi\sqrt{KL}}{\left(1 - \left(\frac{KR^2}{4L}\right)\right)^{\frac{1}{2}}},$$

the form usually quoted if we neglect the second term of the denominator.

I purpose to show that in a discharge of the sort here contemplated (which has been shown to be the result of the ordinary premisses given at page 425) there will be no work done by any electromotive force which lags at an angle β behind the current, provided the initial condition is one of zero-current. And, further, that the source of E.M.F., which is represented by the side of the isosceles triangle in advance by the angle β, of the effective E.M.F., does all the work of heating the circuit and no more. It will thus be seen that there is *no provision in the theory for expenditure of power in the field*, and hence that the theory does not explain the well recognized phenomenon of radiation into space.

To establish the above-mentioned propositions, take the product of the projections of two lines undergoing variations corresponding to the two radii vectores of two equiangular spirals of the same characteristic angle β and period, and differing in phase by the angle 2γ.

One of these quantities may be expressed by

$$a e^{-\frac{\theta+\gamma}{\tan\beta}} \sin \overline{\theta+\gamma}.$$

The other by

$$b e^{-\frac{\overline{\theta-\gamma}}{\tan\beta}} \sin \overline{\theta-\gamma}.$$

The product is

$$ab \,.\, e^{-\frac{2\theta}{\tan\beta}} \sin \overline{\theta+\gamma} \sin \overline{\theta-\gamma},$$

or

$$ab \,.\, e^{-\frac{2\theta}{\tan\beta}} (\sin^2\theta - \sin^2\gamma).$$

This quantity, multiplied into an element of time dt, has to be integrated through one period. Since $\frac{d\theta}{dt} = \frac{2\pi}{t_2}$, the integral I becomes

$$\frac{abt_2}{4\pi}\int e^{-\frac{2\theta}{\tan\beta}} (\cos 2\gamma - \cos 2\theta)\, d\theta,$$

or

$$\frac{abt_2}{4\pi}\int e^{-\frac{2\theta}{\tan\beta}} \cos 2\gamma\, d\theta - \frac{abt_2}{4\pi}\int e^{-\frac{2\theta}{\tan\beta}} \cos 2\theta\, d\theta.$$

The first term of the integral is

$$-\frac{abt_2}{8\pi} \cos 2\gamma \tan\beta\, e^{-\frac{2\theta}{\tan\beta}}.$$

The second term is

$$\frac{abt_2}{8\pi} \sin\beta \cos \overline{\beta+2\theta}\, e^{-\frac{2\theta}{\tan\beta}};$$

and therefore the integral is expressed :—

$$\mathrm{I} = \frac{abt_2}{8\pi} e^{-\frac{2\theta}{\tan\beta}} \{\sin\beta \cos \overline{\beta+2\theta} - \tan\beta \cos 2\gamma\}.$$

This expression has to be taken between limits. If we contemplate one revolution only the limits will be $\Theta_1 + 2\pi$ and θ_1, and the Definite Integral becomes

$$\frac{abt_2}{8\pi}\{-\sin\beta \cos \overline{\beta+2\theta_1} + \tan\beta \cos 2\gamma\} e^{-\frac{2\theta_1}{\tan\beta}} \left(1 - e^{-\frac{4\pi}{\tan\beta}}\right).$$

If the limits are infinity and θ_1 the integral becomes

$$\frac{abt_2}{8\pi}\{\tan\beta \cos 2\gamma - \sin\beta \cos \overline{\beta+2\theta_1}\} e^{-\frac{2\theta_1}{\tan\beta}} \quad . \quad (\alpha)$$

Either of these expressions becomes zero when

$$\tan\beta \cos 2\gamma = \sin\beta \cos \overline{\beta+2\theta_1}$$

or

$$\cos 2\gamma = \cos\beta \cos \overline{\beta + 2\theta_1},$$

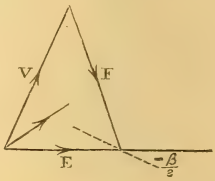
showing that the condition that no work shall be done in the electric problem depends on the initial circumstances, *i. e.* θ_1 is involved. If $2\gamma = \beta$ the condition of no work becomes

$$\cos \overline{\beta + 2\theta_1} = 1,$$

which is satisfied when

$$\theta_1 = -\frac{\beta}{2}.$$

Hence if the initial condition be that of no current, the line bisecting the angle between the line of effective E.M.F. and that of the self-induced E.M.F. makes $-\frac{\beta}{2}$ with the line $\theta = 0$, and it is thus proved that on the whole no work is done in the field.



If, on the other hand, we make

$$\theta_1 = +\frac{\beta}{2},$$

and start from a point where the current is zero, we have in the above expression, when proper substitutions are made for a and b, the value of the work done on the circuit by the discharging condenser. The integral between infinity and θ_1 becomes, when $\theta_1 = \frac{\beta}{2}$ and $2\gamma = \beta$,

$$\frac{ab \,.\, t_2}{8\pi}\{1 - \cos 2\beta\} \sin\beta \,.\, e^{-\frac{\beta}{\tan\beta}},$$

or

$$\frac{ab \,.\, t_2}{4\pi} \sin^3\beta\, e^{-\frac{\beta}{\tan\beta}}.$$

In this case $b = \frac{E}{R}$ and $ae^{-\frac{\beta}{\tan\beta}} \sin\beta$ is the potential difference between the plates of the condenser at starting $= V_1$, say, $= V \sin\beta$. Hence the expression becomes

$$\frac{E}{R} \cdot \frac{t_2}{4\pi} \sin^3\beta \,.\, V$$

(E and V being now the full sides of the triangle, properly interpreted), and $\frac{E}{2 \,.\, V} = \cos\beta$ by the geometry of the triangle, and further,

$$\tan\beta = \frac{2\pi t_1}{t_2} \text{ and therefore } \frac{t_2}{4\pi} = \frac{t_1}{2\tan\beta},$$

and the work

$$= \frac{E^2}{R}\,\frac{1}{2\cos\beta}\,\frac{t_1}{2\tan\beta}\sin^3\beta, \text{ or } \frac{E^2}{R}\,\frac{t_1\sin^2\beta}{4},$$

which is the expression we should obtain if we integrate the square of the current multiplied by Rdt, seen as follows:—

In the general expression (α) obtained above for the product of the projections make $a = E$, $b = \frac{E}{R}$, and $\theta_1 = 0$, $\gamma = 0$ the expression (α) becomes

$$\frac{E^2 t_2}{8\pi R}\{\tan\beta - \sin\beta\cos\beta\},$$

or

$$\frac{E^2}{4R}\cdot\frac{t_1}{\tan\beta}\{\tan\beta - \sin\beta\cos\beta\},$$

or

$$\frac{E^2}{4R}\,t_1\sin^2\beta, \text{ as above.}$$

Thus the whole of the work goes to heat the wire, and, further, substituting in the equation for E in terms of V, it may be shown to be entirely derived from the charged condenser.

The work may be written, eliminating E,

$$\frac{2V^2\cos\beta}{R}\,\frac{t_2}{4\pi}\sin^3\beta,$$

or

$$\frac{V^2}{R}\,\frac{t_1}{\tan\beta}\cos\beta\sin^3\beta.$$

Now $V_1^2 = V^2\sin^2\beta$, and thus the work is

$$V_1^2\frac{t_1}{R}\cos^2\beta,$$

or, since $\cos^2\beta = \frac{t_3}{t_1}$,

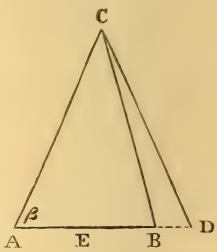
$$= \frac{V_1^2 t_3}{R}, \text{ and } t_3 = \frac{KR}{2}$$

$$= \frac{V_1^2 K}{2},$$

which is the ordinary expression for the energy stored in the condenser; and this appears from the investigation to be

entirely expended in heating the circuit, and there is no margin for the exhibition of power elsewhere.

Suppose a line A B to represent (E) the line of effective E.M.F. At the extremity A set off A C as the direction of the line representing the P.D. of the condenser.



Then, as the condenser contains all the energy that is going to be expended on the circuit and on the æther, from what has been said it is clear that A C must be rather longer than the side of the isosceles triangle; for, if not, the energy stored will not do more than heat the circuit. If therefore a perpendicular be dropped upon A B from C, it will fall at a point nearer B than A.

Join C B, and, further, draw C D to meet A B produced in D, and so that C D A is an isosceles triangle on A D as base, and therefore C D A $=\beta$. Now C B must be the line representing the resultant of the induced electromotive forces F, and however complicated the case may be this line C B is equivalent to two components C D, D B; of which C D results in no expenditure of power because it is in a phase β *behind* the current, and D B is in phase directly opposed to the current, and therefore resulting in whatever expenditure of energy takes place outside the circuit, and therefore in the æther or in magnetic bodies, or in neighbouring or surrounding conductors. As in the former case of sustained oscillations, it may be shown that B C D is a *magnetic lag* necessary for the exhibition of such phenomena.

The electromotive force D B may be expressed by $-\lambda C$ as before, and the general equation

$$V+F=E$$

takes the form

$$V-L\frac{dC}{dt}-\lambda C=RC,$$

and, as this may be written

$$V-L\frac{dC}{dt}=(R+\lambda)C,$$

we see that the extra consideration required to express the actual state of things is simply that the resistance of the circuit is virtually increased. In the previous work it is necessary to write $(R+\lambda)$ in all the equations.

The actual work done altogether is derived from the charged condenser. This is divided between the circuit and the field in the ratio $R:\lambda$.

It may happen, therefore, that if the circumstances of the discharge are such as to make λ very large in comparison with R, the ordinary heating-effect may be minimized. Among such causes is frequency, and in this consideration is to be found the true explanation of some of the experiments of M. Nikola Tesla. The energy of the discharges which that physicist encountered was expended in chief part in radiation which his body did not check, and not in current through his body. It is here suggested that the best way to measure radiation would be to measure the *defect* in the heating of a circuit, taking care to note the P.D. of the condenser at the moment previous to discharge.

In ordinary *sustained* oscillations, as derived from a machine, the alternations are not of sufficient frequency to make the effect of λ perceptible. Electromotive forces of induction involve the period in their denominators, and it is reasonable to suppose that induced magnetic fields do the same; and if the period of the electromagnetic vibrations becomes comparable with that of light, it is conceivable that mere heating might vanish, as in the solar spectrum light has less heating-effect than radiation of smaller frequency from the same source.

XLI. *Note on the Heat of Vaporization of Liquid Hydrochloric Acid. By* K. Tsuruta, *Rigakushi, Tokio, Japan**.

In the thirtieth volume of the Proceedings of the Royal Society of London Mr. Ansdell gave a full account of a series of experiments on the condensation of hydrochloric acid. At the end of the paper he promises another communication containing his considerations on some thermodynamical quantities relating to that gas, but this, so far as I am aware, has never appeared. Although his measurements have often been referred to and used by other physicists, yet some of the deductions that can be made from them appear still left untouched, for instance the heat of vaporization, which forms the subject of this note.

For the sake of convenience of reference I here reproduce those measurements as contained in the following Table given by Ansdell :—

* Communicated by the Author.

	A.	B.	C.	D.	E.	F.
1.	4°	137·31	$\frac{1}{38·89}$	7·55	18·18	29·8
2.	9·25	118·96	$\frac{1}{45·75}$	7·90	15·05	33·9
3.	13·8	103·50	$\frac{1}{53·19}$	8·35	12·39	37·75
4.	18·1	91·77	$\frac{1}{61·17}$	8·74	10·50	41·80
5.	22	81·19	$\frac{1}{70·06}$	9·10	8·92	45·75
6.	26·75	69·69	$\frac{1}{82·94}$	9·50	7·33	51·00
7.	33·4	55·75	$\frac{1}{105·98}$	10·12	5·50	58·85
8.	39·4	44·85	$\frac{1}{134·33}$	10·68	4·19	66·95
9.	44·8	36·34	$\frac{1}{168·67}$	11·96	3·03	75·20
10.	48	31·33	$\frac{1}{197·60}$	12·00	2·61	80·80
11.	49·4	27·64	$\frac{1}{224·96}$	12·92	2·13	84·75
12.	50·56	25·70	.....	14·30	1·79	85·33
13.	51	23·96				

The column A gives the temperature of the gas.

The column B gives the volume of the saturated vapour at point of liquefaction.

The column C gives the fractional volume of the gas at point of liquefaction in relation to the initial volume under one atmospheric pressure.

The column D gives the volume of the condensed liquid.

The column E gives the ratio of the volume of the gas to that of the liquid.

The column F gives the pressure in atmospheres.

These data alone are incomplete to enable us at once to deduce by calculation the heat of vaporization in terms of the usual units (metre and kilogramme). Here are given only the relative volumes of the saturated vapour and condensed liquid, so that their specific volumes at different temperatures, which are wanted, are unknown. It will, however, be enough for our purpose if we know their densities. Now, Ansdell gave as results of independent measurements the densities of the condensed liquid at different temperatures. An interpolation formula, obtained between those densities

and those temperatures, when combined with the numbers given in the second and fourth columns of the above Table, will enable us to find the corresponding densities of the saturated vapour. The results thus found were not very satisfactory. Another way to overcome the difficulty is to make use of the numbers in the third column, which give the volumes of the saturated vapour just at the point of liquefaction in relation to the volume occupied by the mass of the gas at the temperature t° (column A*) and under the pressure of one atmosphere. If the specific volume of the gas under the normal circumstances be known in terms of the usual units, this together with the coefficient of expansion under that pressure will give us the specific volumes of the saturated vapour at different temperatures. Now, Biot and Arago † give the density of hydrochloric acid under the normal circumstances to be 1·2474 in reference to air. Therefore, the specific volumes under consideration will be given by the following :—

$$s = \frac{1}{1{\cdot}293} \cdot \frac{1}{1{\cdot}247} \cdot \begin{bmatrix}\text{fractional}\\ \text{volume}\end{bmatrix} \cdot (1+\alpha t).$$

When a long time ago I began my calculation I was not able to get any information with respect to the coefficient of expansion, and I assumed it perhaps not far from the value 0·003665. Quite recently, however, I have found that it was determined by Regnault ‡ as long ago as 1843 to be 0·003681, and so I have proceeded to recalculate. Of course no great differences were thus wrought in the final values of the heat of vaporization. It is, moreover, to be remarked that Regnault himself did not put much confidence in the accuracy of his value on account of an unavoidable admixture of air, very small though it was, with the gas he investigated.

The formula for the heat of vaporization (according to the notation of Clausius) becomes :—

$$r = \frac{10333}{425} \cdot \frac{1}{1{\cdot}293} \cdot \frac{1}{1{\cdot}247} \cdot \begin{bmatrix}\text{fractional}\\ \text{volume}\end{bmatrix} \cdot (1+\alpha t) \cdot \left(1-\frac{\sigma}{s}\right) \cdot \frac{dp}{dT} \cdot T,$$

in which the ratio σ/s is to be supplied by the numbers in the second and fourth columns of the above Table.

* As it must have been, although it is not explicitly mentioned.
† Wüllner, *Lehrbuch der Physik*, iii. p. 150.
‡ *Ann. de Chimie et Physique*, série 3, tome iv.

$\frac{dp}{dT}$ was calculated from the following interpolation formula found by the method of least squares :—

$$p = 28{\cdot}451 + 0{\cdot}4914\,t + 0{\cdot}012463\,t^2,$$

in the evaluation of whose constants the numbers in the eleventh row in the above Table were omitted, because the representative point in the p- and t-curve was much out of the general course. p (calculated) in the following Table are from the above interpolation formula, whose use is amply justified by the numbers in the difference-column.

	t.	p (observed).	p (calculated).	Difference.	r.
		atm.	atm.		calor.
1.	4°	29·8	30·61	+0·81	61·02
2.	9·25	33·9	34·10	+0·20	64·99
3.	13·8	37·75	37·60	−0·15	65·77
4.	18·1	41·8	41·43	−0·37	65·43
5.	22	45·75	45·29	−0·46	63·51
6.	26·75	51	50·57	−0·43	60·02
7.	33·4	58·85	58·76	−0·09	53·17
8.	39·4	66·95	67·15	+0·20	45·18
9.	44·8	75·2	75·47	+0·27	35·79
10.	48	80·8	80·75	−0·05	30·08
11.	49·4	84·75	83·14	−1·61	23·49
12.	50·56	85·33	85·22	−0·11	
13.	51				

The manner of variation of these numbers for r, as deduced from the observations of Ansdell, is very remarkable. From 4° to about 14° the heat of vaporization increases, attains there a maximum value, then decreases in a regular manner, but from about 45° onwards it diminishes quite rapidly, as if the gas were preparing for the critical point (51°·25), at which the heat of vaporization is to vanish.

Among those substances whose heat of vaporization was investigated by MM. Cailletet and Mathias * we have no instance like hydrochloric acid. It is much to be desired that any one who has proper instruments in his possession will take the trouble to decide whether the anomaly is real or whether there were some mistakes in our data.

* *Journ. de Physique*, tom. v. 2e série, 1886. Also, *ibid.* tom. ix. 2e série, 1890.

XLII. *Note on the Flow of Water in a Straight Pipe.* *By* M. P. Rudski, *Priv. Doc. in the University of Odessa* *.

It is a known fact that the law of resistance to the motion of a liquid in pipes and channels of great size differs much from that in capillary tubes. It is also known that this difference is due to the presence of eddies in great pipes, while in capillary tubes the liquid flows in straight lines. Prof. Osborne Reynolds † has shown that there exists a certain critical mean velocity, depending on the diameter of the pipe and on the temperature (*i. e.* viscosity) at which the eddies must appear. He thinks that the appearance of eddies is due to the instability of rectilineal motion. But Lord Kelvin ‡ has shown that at least for small disturbances the rectilineal motion is stable provided the coefficient of viscosity is not zero. Although Lord Rayleigh § thinks that Lord Kelvin's proof is not quite convincing, it seems to me to be so, because the steady rectilineal motion with zero velocity at the walls satisfies the condition that the loss of energy shall be the least possible. This motion belongs to the type which was shown by Helmholtz to have this property ‖. Now it is known that generally the motions, which in a certain manner satisfy the minimum or maximum condition, are stable.

The same question was also treated by Mr. Basset ¶. He has found the rectilineal motion unstable. As far as I can understand him, from a short communication, it was only after he had introduced in the expression of resistance a term depending on the square of relative velocity. In doing so he has anticipated the law of resistance proper to the eddying motion. On the other hand, he finds that without this term the steady rectilineal motion remains always stable. His results also agree closely with the results of Lord Kelvin.

It seems to me that all this clearly agrees in showing that it is not the question of stability or instability which arises here, but another one. In speaking of stability we mean *eo ipso* the tacit assumption that the eddying motion may be also expressed with the help of functions satisfying the common partial differential equations of viscous fluid

* Communicated by the Author.
† Phil. Trans. 1883, p. 935.
‡ Phil. Mag. 5 ser. xxiv. pp. 188 and 272.
§ Phil. Mag. 5 ser. xxxiv. p. 67.
‖ Basset, Hydrodynamics, vol. ii. p. 356.
¶ Proceedings Roy. Soc. vol. lii. no. 317, p. 273.

motion. Our equations of disturbed motion serving to investigate the question of stability are the same hydrodynamical equations with certain terms neglected. These equations, as Lord Kelvin has proved, show that the undisturbed motion is stable. But if we introduce something that is not contained in the hydrodynamical equations, as Mr. Basset has done, we find the sought instability.

In other words, our hydrodynamical equations, which we know to be strictly true only for small relative velocities, are now shown to be, in the case of water, of very limited importance. They are not able to express the eddying motion.

In the motion which they are able to express, any surface drawn within the liquid is supposed to be strained in a continuous manner. In the eddying motion these surfaces are continually breaking and again reforming, an opinion which seems not to be new to hydraulicians *.

The opinion that it is with a real breaking that we have to do is strongly supported by a striking fact observed by Prof. Reynolds. The eddies appear only at a certain distance from the entrance of the pipe. This distance is diminishing when the velocity increases, but diminishes asymptotically. Now it is a known fact that the breaking of bodies, solid, plastic, or plastico-viscous, depends not only on the amount of the strain, but also on the velocity of straining. Even hard bodies sustain a great strain when the straining is slow enough; on the other hand, *flexible* bodies, when very rapidly strained, break down.

On the other hand, when the liquid enters the pipe tumultuously, but with small mean velocity, the viscosity begins to act at advantage, the breaking ceases, and the eddies die out. Reynolds has shown that this reversal from tumultuous to quiet motion occurs at a critical mean velocity, which *ceteris paribus* is about 6·3 times smaller than the other mean velocity which renders the quiet motion impossible.

All other features of the phenomenon—the dependence of critical mean velocity, *i.e.* of the critical rate of straining, on the viscosity and on the size of the tube—are clearly in best accord with the hypothesis of breaking for a certain critical rate of straining.

The existence of two critical velocities—a greater which makes the quiet motion impossible, and a smaller which makes the tumultuous motion impossible—is very interesting, and shows similitude to many other physical phenomena.

* See Boussinesq, "Essai sur la théorie des eaux courantes," *Mém. Sav. Etr.* vol. xxiii. p. 5.

XLIII. *Liquid Friction.* By JOHN PERRY, *F.R.S.*, *assisted by* J. GRAHAM, *B.A.*, *and* C. W. HEATH*.

[Plate VII.]

A PIECE of apparatus such as is used in this investigation was designed and partly constructed in Japan in 1876; it is described in my book on Practical Mechanics (1883). The specimen actually used by us was constructed at the Finsbury Technical College in 1882, and has been occasionally used since that time, but no complete sets of observations were attempted till October 1891.

The simplest hydrodynamical condition of viscous fluid is that of the fluid bounded by two infinite parallel planes, the fluid in one boundary being at rest, the velocity in the other boundary being constant and in the plane. Motions in a pipe and near a vibrating disk, or even near a steadily rotating disk, are rather complicated. Our apparatus was designed to approach as nearly as possible to the conditions subsisting between the infinite planes. Between two such planes, if V is the constant velocity of one of them, the other being at rest, and b is their distance asunder, the fluid being of uniform density, and gravity being neglected, if z is measured at right angles from the fixed plane, the equation of steady motion is

$$\frac{d^2v}{dz^2} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$v = \mathrm{V}z/b\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the tractive force per unit area required at the moving plane to maintain the motion is $\mu\mathrm{V}/b$, where μ is the coefficient of viscosity. We have used, instead of planes, concentric cylindric surfaces of as large radii and as small difference in radii as could be conveniently constructed and used (see Pl. VII. fig. 2).

E E E is a cylindric trough, of which the curved parts E and E are brass. The inner and outer radii of this trough are 10·39 and 12·65 centimetres. C, which forms the bottom, is of iron; and the whole trough can be rotated about its vertical axis at any desired speed by driving the pulley P from a coned pulley D with numerous steps.

G is a hollow brass cylinder supported by a steel wire L, of 0·037 centim. diameter, 67·78 centim. long, whose axis coincides with the axis of the trough and the axis of

* Communicated by the Physical Society: read March 24, 1893.

rotation. G may be raised or lowered relatively to the trough. The outer radius of G is 11·63 centim., the inner being 11·41 centim. The whole apparatus is supported on a stand, with three adjustable feet. We exhibit also some photographs of the apparatus in position, showing how it was driven.

The trough contains the liquid whose viscosity is to be measured: when it rotates, G tends to rotate; and when for any constant speed G is in equilibrium, the twist in the steel wire measures the torque due to the tractive forces with which the liquid acts upon G at its inner and outer surfaces. The twist was measured by the angular motion of a pointer clamped on the wire at a distance of 59 centim. from the fixed end.

To test the accuracy of our assumption that the fluid behaved as if between parallel plane surfaces, let us consider the actual motion in which the stream-lines are circles. Consider the motion of a stream-tube of section $\delta r\,\delta x$, x being measured axially and r radially. The tangential force on unit cylindric surface of radius r is $\mu\left(\frac{dv}{dr}-\frac{v}{r}\right)$, if v is the velocity. The moment due to all such forces on the inner surface of our ring is

$$2\pi r^2 . \mu\left(\frac{dv}{dr}-\frac{v}{r}\right)\delta x.$$

The moment tending to increase the velocity of the ring due to forces on the cylindric parts of it is therefore

$$2\pi\mu . r^2\left(\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}\right)\delta r . \delta x;$$

also, due to the plane faces we have the moment

$$2\pi\mu r^2\frac{d^2v}{dx^2}\delta r . \delta x.$$

Equating the sum of these to the rate of increase of the moment of momentum of the ring, we have

$$\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}+\frac{d^2v}{dx^2}=\frac{\rho}{u}\frac{dv}{dt} \quad . \quad . \quad . \quad . \quad (3)$$

as the equation of motion in co-axial circular stream-lines.

Now the discontinuity at the edge, and also the nearness of the bottom of the trough, cause the term $\frac{d^2v}{dx^2}$ to be important; but the solution seems to be very difficult. Maxwell satisfied himself (Collected Papers, vol. ii. pp. 16–18) that the discontinuity at the edge of a vibrating disk could be allowed

for as a virtual increase in the radius of his disk, and the assumption that the behaviour of his fluid was the same as if his disk were part of an infinite disk. The correction not being readily obtained for a disk, he assumed it to be the same as for the straight edge of an infinite plane surface. We are certainly not less correct in taking the same correction for the edge of our cylinder *. Following Maxwell, therefore, we assumed that when our cylinder G was immersed to the depth AB or l in the fluid it was really a portion of length $l+\lambda$ of an infinite cylinder of the same diameter. We therefore neglect $\frac{d^2v}{dx^2}$ in (3), and we use

$$\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}=\frac{\rho}{\mu}\frac{dv}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the motion is steady, that is when $dv/dt=0$, the solution is

$$v = \mathrm{A}r+\mathrm{B}/r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If $v=v_1$ when $r=\mathrm{R}_1$, and $v=0$ when $\mathrm{R}=\mathrm{R}_2$, then

$$v = v_1\mathrm{R}_1(r-\mathrm{R}_2^2/r)/(\mathrm{R}_1^2-\mathrm{R}_2^2).$$

We must now distinguish between the space outside the suspended cylinder and the space inside it. The radii of the inner and outer surfaces of the suspended cylinder are 11·41 and 11·63 centim., and the inner and outer radii of the trough are 10·39 and 12·65 centim.

Our cylindric surfaces were not perfectly true, although great care was taken to make them so; and the radii given are only average dimensions. But, inasmuch as slightly tilting the apparatus or otherwise putting the axis of the suspended cylinder out of coincidence with the axis of the trough made only small differences in the observations, we did not think that such inaccuracies of workmanship or measurement as existed could affect our results.

Even when the tilting of the apparatus was quite evident to the eye, the tractive torque was found to be only slightly increased by the tilting. Of course, as the suspended cylinder

* It is to be remarked that Maxwell assumed, generally, that there was no radial motion of his fluid. Now there must have been radial motion, his disks resembling centrifugal fans in their action, creating a variable flow always outwards between his fixed and moving disks; and the energy wasted in producing this flow is neglected by him. We do not know the amount of this error, and he may have satisfied himself as to its insignificance. Prof. Maurice FitzGerald in criticizing this proof has pointed out the fact that on James Thomson's theory of river bends there must exist a radial motion of an interesting kind in our apparatus.

got closer and closer to the side of the trough the torque did increase, and became very large when the suspended cylinder nearly touched the side of the trough.

Again, it was observed that at our highest speeds the amount of wetted surface did not perceptibly alter; and we are, we think, justified in assuming that the surface of the liquid was always a plane surface.

It is evident that the tractive forces on the suspended cylinder are the same whether we assume the trough to revolve steadily at ω radians per second, the suspended cylinder being at rest, or the suspended cylinder to revolve steadily at ω radians per second and the trough to remain at rest. We shall therefore, for ease of calculation, always assume the trough to be at rest and the suspended cylinder to be revolving at ω radians per second. Then the velocities of its inner and outer surfaces are, in centimetres per second, $11{\cdot}41\omega$ and $11{\cdot}63\omega$.

On any cylindric surface the tractive force per unit area being $\mu\left(\frac{dv}{dr}-\frac{v}{r}\right)$ is $-\frac{2B}{r^2}\mu$ from (5); so that, whether for the outer or inner space, if R_1 is the radius of the suspended moving cylindric surface, and R_2 the radius of the fixed surface, the tractive moment per centim. of length is

$$\pm 4\pi\omega\mu R_1^2/(R_1^2/R_2^2-1).$$

Taking actual sizes, this is 0·5 per cent. greater than the value obtained by calculating the forces on the assumption that the fluid moves in plane layers as in (2), b being the actual thickness of fluid 1·02 centim., and V being the actual velocity at the mean radius. We may, in fact, imagine the speeds to be increased by 0·5 per cent., and make all calculations as to viscosity on the assumption of motion in plane layers.

The tractive torque per centimetre of length of cylinder is, in our case, $19010\mu\omega$, or $1991n\mu$ if the angular velocity is given as n turns per minute. If l is the wetted length in centimetres, and λ is the virtual additional length representing the edge effect, the total torque is $1991n\mu(l+\lambda)$. The total observed motion of the pointer being D degrees, and the torque per degree being a, the torque due to tractive forces acting on the cylinder is

$$aD = 1991\,n\mu(l+\lambda)\ ;$$

and if this law is found to be true experimentally, then

$$\mu = aD/\{1991(l+\lambda)n\}. \quad . \quad . \quad . \quad . \quad (6)$$

Two methods of determining the torsional constant of the wire were employed :—

First Method.—A fine cotton thread was wound round the outside of the suspended cylinder and passed over a nearly frictionless pulley (the pulley of an Attwood's machine) to a scale-pan. The thread was nearly horizontal as it left the cylinder. In this way it was found that the twisting moment required to produce a pointer-rotation of one degree was 1531 dyne-centimetres. In making the measurement as the weight of the scale-pan and its contents was gradually increased, the steel wire was drawn away from the vertical, and therefore from the middle of the scale; but the stand was tilted to counteract this effect.

The effects due to solid friction were eliminated by taking the mean of the limiting weights for equilibrium. When the weight was 30 grams, one tenth of a gram either added to or taken from the scale-pan produced a perceptible change in the position of the pointer ; so that the solid friction was small.

Second Method.—The suspended cylinder was allowed to vibrate, twisting and untwisting the wire ; and its times of oscillation were noted. The observations were repeated when a known moment of inertia had been added. Unloaded, it made 40 complete oscillations in 583 seconds, or one oscillation in 14·575 seconds. We then attached to the cylinder an iron bar of rectangular section, whose own moment of inertia had been determined accurately by previous experiments (found to agree with calculation on the assumption that it was homogeneous), this moment of inertia being 566·2 (in gram-centimetre^2 units). The time of a complete oscillation was now found to be 21·425 seconds. It follows that the moment of inertia of the suspended cylinder is 487·72, and the torsional constant of the wire is readily obtained. This constant being corrected on account of the position of the pointer, it follows that to produce a rotation of the pointer of one degree requires a torque of 1552 dyne-centimetres. This is greater than the constant derived from direct measurement by $1\frac{1}{3}$ per cent.; but, on the whole, we are rather inclined to accept the number obtained directly, as we are not quite sure that the mean position of the iron bar was at right angles to the magnetic meridian.

Eight quite independent measurements of the diameter of the wire were made by men experienced in making such measurements ; and the mean value was ·0371 inch, the greatest and least being ·0373 and ·0369. Using this mean value, and the directly measured torsional constant, it would seem that the modulus of rigidity of the steel is $7{\cdot}71 \times 10^{11}$.

As an error of ·0004 inch in the diameter measurement leads to an error of 4 per cent. in the modulus of rigidity, and as the modulus of rigidity usually taken for steel is $8{\cdot}19 \times 10^{11}$, we believe that our constant 1531, as directly measured, is sufficiently correct for practical purposes.

In using (6), then, we take a to be 1531.

The virtual addition λ ought, by Maxwell's formula, to be 0·52 centim. in our case. But the bottom of the trough H was only 0·5 centim. from the edge B of the suspended cylinder in most of our experiments, and we do not know how to calculate for this. Our experiments have shown that when this distance is 0·5 centim. the twisting moment at a given speed is practically the same as when the distance is much greater; but we did not know this from any theory, and, besides, it is always rather dangerous to depend upon a theoretical calculation of λ such as Maxwell was compelled to use. It is possible, also, that a correction of the same kind ought to be introduced for capillary and other actions at the surface of the liquid. The action of the atmosphere was in any case negligible, because when there was no liquid present in the trough, so that there was an action of the air several times greater than ever occurred during the experiments, the deflexion was quite imperceptible at much higher speeds than those used in the experiments.

The temperature being kept as nearly as possible constant, but probably varying between 18°·9 C. and 20°·1 C. (stated as 19°·5 C.), the following experiments were made with sperm-oil, beginning with a small quantity in the trough and ending with a large quantity. The bottom of the trough was in every case 0·5 centim. below the edge of the suspended cylinder.

TABLE I.—June 9th, 1892.

n.	Deflexion D when				
	l=0·5 cm.	l=2·5 cm.	l=5 cm.	l=7·5 cm.	l=9·9 cm.
50	24	67	112	158	
49	...	...	...	...	196
48					
40	18	...	...	132	163
39	...	53	91		
23	10				
17·5	8	..	...	57	73·5
17	...	24	39		
12	5	...	...	40	
11·5	...	16	27		
11	...	...	...	...	49

As the deflexion is sufficiently nearly proportional to the speed to allow of corrections by this rule when the corrections are small, we have corrected the above observations to the speeds 50, 40, $17\frac{1}{2}$, $11\frac{1}{2}$; and we obtain the following results :—

Values of l.	Values of n.			
	50.	40.	$17\frac{1}{2}$.	$11\frac{1}{2}$.
·5	24	18	8	5
2·5	67	54	25	16
5·0	112	93	40	27
7·5	165	132	57	$38\frac{1}{2}$
9·9	200	163	73·5	51

D and l were then plotted as the coordinates of points on squared paper; and it was obvious that for each value of n these points lay very nearly in a straight line, and all the straight lines passed through the point $l=-0{\cdot}8$. It is curious that the linear law should hold for such small values of l as 0·5 centim., and for high speeds as well as low speeds. We shall presently see that some of these speeds are considerably above the critical speed at which (4) ceases to represent the motion.

We may take it, then, that $\lambda=0{\cdot}8$ centim., which is greater than the calculated value 0·52. The discrepance cannot be due to the distance BH being small, for we have altered this distance and found no perceptibly different results. As already stated, it may be due to some capillary surface action. Taking $a=1531$ and $\lambda=0{\cdot}8$, we have (6) becoming

$$\mu = 0{\cdot}769\,\mathrm{D}/n(l+0{\cdot}8). \quad . \quad . \quad . \quad . \quad (7)$$

Of course our results are consistent with our equations of motion only so long as $\mathrm{D}/(l+0{\cdot}8)$ is proportional to n.

Many observations have been made with this apparatus during the last year on various liquids, under very different conditions of temperature and speed and depth. We give here a set made on sperm-oil. In all cases the bottom of the trough was 0·5 centim. below the edge of the suspended cylinder.

Keeping the oil at a constant temperature we ran the trough at a number of speeds, and repeated at other constant temperatures. The results are given in Tables IV. to XI.

When a temperature had to be taken the rotation was stopped and a thermometer dipped about halfway down in the oil, the reading being taken at the end of about half a minute.

A small Bunsen flame was applied underneath the trough when a temperature higher than the room had to be maintained for a considerable length of time.

As the temperature varied slightly, and we wished to reduce our observations to constant temperatures, we afterwards made two sets of observations at very varying temperatures but constant speeds. These later observations we shall consider first. They are given in Tables II. and III.

TABLE II.—March 29th, 1892. ($l=8{\cdot}275$ centim.)

n.	$\theta°$ C.	D.	$\frac{40}{n}\frac{D}{l+\lambda}$.	μ.	μ calculated.
39·5	13·5	189	21·09	·400	·446
39·5	17·1	165	17·60	·334	·357
40	19·5	150	16·53	·318	·317
40	24·0	134	14·77	·287	·266
40	25·3	126·5	13·94	·268	·254
40	28·9	111·5	12·28	·236	·228
40	32·0	109	11·46		
40	42·5	88	9·70		
40	46·9	81	8·65		
40	58·5	67	7·11		
40	64·0	58	6·39		
40	71·0	56	6·17		
40	77·0	50	5·51		
40	85·5	46·5	5·12		

The numbers in the column headed $\frac{40}{n}\frac{D}{l+\lambda}$ are obviously intended to be corrections of $D/(l+\lambda)$ for the constant speed of 40 revolutions per minute.

TABLE III.—March 30th, 1892. ($l=7{\cdot}78$ centim.)

n.	$\theta°$ C.	D.	$\frac{9}{n}\frac{D}{l+\lambda}$.	μ.	μ calculated.
8·75	5·2	160	19·19	1·64	2·06
9·75	8·0	85	9·15	0·78	0·82
9·2	10·0	57	6·56	0·73	0·62
9·0	10·8	47	5·48	0·47	0·56
9·0	16·6	36·5	4·26	0·363	0·366
9·2	24·8	26·5	3·02	0·258	0·259
9·0	35·0	19·5	2·27	0·194	0·196
9·0	47·0	14·0	1·63	0·139	0·137
9·0	56·5	10·2	1·19	0·101	0·104
9·0	67·0	8·0	0·93	0·079	0·081
9·0	89·0	5·4	0·63	0·060	0·058
9·0	84·5	6·0	0·70	0·054	0·054

The numbers headed $\frac{9}{n}\frac{D}{l+\lambda}$ are intended to be corrections of $D/(l+\lambda)$ for the constant speed of 9 revolutions per minute.

We have plotted the numbers in the last columns of these tables with θ upon a sheet of squared paper; but it is unnecessary to publish the resulting curves. We exhibit them to the members of the Society.

Knowing what has been done by Prof. Osborne Reynolds, it seemed unlikely that one simple formula should satisfy either of these curves; that is, it was likely that in the lower curve there was some temperature for which the speed $n=9$ was a critical speed, and there was also a temperature for which $n=40$ was a critical speed. We therefore used the curves merely for small temperature-corrections in our other experiments, in which we kept the temperature nearly constant.

It was therefore without much interest that, in preparing this paper for publication, we tried to obtain empirical formulæ for these curves; and at first we used, not the observations themselves, but the observations as corrected by curves drawn upon squared paper.

When $\log(\theta-4{\cdot}2)$ and $\log\frac{D}{l+\lambda}$ are plotted as coordinates of points on squared paper, we were astonished to find that when $n=9$ the points lie in two straight lines. The allineation of the points is very striking, even when the uncorrected observations are taken, and leads to the following empirical formula:—

Letting ϕ denote $\theta-4{\cdot}2$, and letting y denote $D/(l+\lambda)$ the torque as measured in degrees deflexion of pointer per unit length of wetted cylinder; then, at the constant speed of $n=9$,

$$y\phi^{1\cdot349}=\text{constant for temperatures above } 40^\circ \text{ C.}$$

$$y\phi^{0\cdot686}=\text{constant for temperatures below } 40^\circ \text{ C.}$$

On plotting $\log y$ and $\log\phi$ for the constant speed $n=40$, the points are not found to lie so nicely in straight lines, but there does seem to be some sort of discontinuity at a temperature of about 45° C.

At first we thought that these temperatures were the temperatures at which the speeds $n=9$ and $n=40$ were the critical speeds, and we were greatly concerned because our result seemed to be quite out of accord with the reasoning of

Prof. Osborne Reynolds *. As his ingenious theory has been completely verified by experiments made upon the very smallest and largest pipes with flowing water, and as it is simple we had adopted it for the reduction of our experiments.

According to his theory, $\frac{D}{l+\lambda}$ or, as we shall call it, y, ought to be proportional to n until n exceeds a certain value; this value being a function of μ/ρ, where ρ is the density of the fluid. Now the alteration of ρ with temperature in such a liquid as sperm-oil is so small that the error in neglecting it is small in comparison with our errors of experiment.

Neglecting, then, the alterations in ρ, the theory of Prof. Reynolds leads to

$$y = a\mathrm{F}^{2-\kappa}n^{\kappa}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where F is a function of the temperature, n the number of revolutions per minute; where $\kappa=1$ until the critical speed n_c is reached, n_c being proportional to F, and κ having a higher value than 1 for all speeds above the critical; a is a constant. This is on the assumption that Prof. Reynolds's theory would lead to the same result in our case as in his pipes.

Now, in the first place, it seemed absurd that the temperatures for which the speeds 9 and 40 were the critical speeds should be so near to one another as 40° C. and 45° C. But a much more serious consideration was this. According to any reasonable application of the theory to our case, at constant speed, if $y\phi^m$ is constant when the speed is less than the critical speed, and if $y\phi^s$ is constant when the speed is above the critical speed, then s ought to be less than m, whereas 1·349 is about twice 0·686. We came to the conclusion that the point of discontinuity has nothing whatever to do with the critical speed; indeed, we subsequently found it probable that $n=9$ does not become the critical speed until the highest temperature of Table III. is reached.

Using the deflexions in Table III. to determine μ according to (7), we have the results given in column 5 of the Tables. The numbers in column 5 of Table I. are calculated for temperatures lower than 26° C., which is about the temperature at which 40 is the critical speed. In some of the following tables, giving the results of experiments made at various constant temperatures, we have also given values of μ. There

* "An Experimental Investigation of the Circumstances which determine whether the Motion of Water shall be Direct or Sinuous, and of the Law of Resistance in Parallel Channels," by Osborne Reynolds, F.R.S., Phil. Trans. pt. iii. (1883).

is as much consistency in all these results as might have been expected. We lay most weight upon the results given in Table III., which lead to the laws

$$\mu = 2{\cdot}06(\theta - 4{\cdot}2)^{-{\cdot}686} \text{ below } 40^\circ \text{ C.}; \quad . \quad . \quad . \quad (9)$$

$$\mu = 21{\cdot}67(\theta - 4{\cdot}2)^{-1{\cdot}349} \text{ above } 40^\circ \text{ C.} \quad . \quad . \quad . \quad (10)$$

We have searched in books in vain for a mention of a discontinuity in any other physical property of sperm-oil about this temperature; but we have already begun to experiment on its other physical properties, as it is unlikely that there should be a discontinuity in the law for the viscosity alone. At the same time, we may say that our chemical friends see no reason for a confirmation of our belief.

In the tables we give the viscosity as calculated from these formulæ; and it will be seen that they agree well enough with the observed viscosities.

TABLE IV.—March 18th, 1892.

(l=6·15 centim. Temperature Constant, 17°·5 C.)

n.	D.	y, or D÷(l+λ).	μ.
36	114	16·41	·351
39	121	17·41	·344
54	172	24·75	·352
69	245	35·26	
80	300	43·16	
92	345	49·64	
23	74	10·65	·356
16	52	7·48	·360
13	41	5·90	·349
8·75	27	3·98	·349

The column headed μ is $0{\cdot}769\,\mathrm{D}/n(l+\lambda)$, and has no meaning at a speed greater than the critical speed. The critical speed, n_c, is probably about 50. The first three and last four values are probably measurements of μ. The average value of these seven is $\mu = 0{\cdot}351$. Formula (9) would make μ to be 0·349.

Plotting $\log y$ and $\log n$ as the coordinates of points on squared paper, the points lie very nearly in a straight line indicating $y \propto n$ until the critical speed, about $n = 50$, is reached, and for all higher speeds the points lie nearly in another straight line indicating $y \propto n^{1{\cdot}25}$.

TABLE V.—March 21st, 1892. ($l=6{\cdot}075$ centim.)

$\theta°$ C.	n.	D.	y.	μ.
22·5	9·25	24·5	3·40	·283
23·2	11	28·0	3·97	·278
22·7	14·2	37	5·16	·280
22·0	17·2	45	6·15	·279
25·0	27	68	10·19	·277
24·5	23	57	8·41	·281
24·0	32	77	11·20	·269
23·0	90	340	48·00	
22·5	102	410	56·96	
23·0	80	276	38·94	
24·0	72	224	32·58	
24·5	56	169	24·95	
24·0	48	129	18·76	
23·5	43	108	15 42	·278
23·0	38	97	13·69	·277

The column headed y is $D/(l+\lambda)$ corrected to the constant temperature of 24° C. by a correction of about 3 per cent. per degree. The numbers in the last column have no meaning for speeds higher than $n=$about 43. The average value of μ, the viscosity, in the first seven and last two observations is 0·278. Formula (9) would make μ for this temperature 0·266.

Plotting $\log n$ and $\log y$ on squared paper gives points lying nearly in two straight lines, showing that $y \propto n$ to the critical speed $n=$about 43, and above that speed $y \propto n^{1{\cdot}37}$.

TABLE VI.—March 21st, 1892. ($l=6{\cdot}075$ centim.)

$\theta°$ C.	n.	D.	y.
29·5	38	81	11·63
30	43	95	13·82
31	48	114	16·99
30·5	56	134	19·73
30·5	60	147	21·65
30	66	175	25·45

y here means $D/(l+\lambda)$ corrected to the constant temperature of 30° C. by a correction of $2\frac{1}{2}$ per cent. per degree. μ as calculated from (7) would have no meaning, as the critical speed for this temperature is about 28 revolutions per minute, and we give no column headed μ. y is very nearly $\propto n^{1{\cdot}33}$.

TABLE VII.—March 22nd, 1892. ($l=5{\cdot}425$ centim.)

$\theta°$ C.	n.	D.	y.	μ.
56	38	49·5	7·92	
55	42	59	9·20	
55	54	72·5	11·31	
56	58	88	14·13	
56·5	74	116	18·79	
57·5	108	158	26·32	
58·5	29	34	5·78	
56	24	25	4·01	·1282
57	17·5	11	1·81	·0791
57	15·5	14	2·31	·1143
54	15·5	12	1·82	·0903
55	16	14	2·19	·1054

y means $D/(l+\lambda)$ corrected to 56° C. by a correction of $2\frac{1}{2}$ per cent. per degree. The critical speed is probably below $n=24$, and for speeds greater than the critical $y \propto n^{1{\cdot}32}$ nearly. For speeds less than this the average value of μ is 0·103. According to (9) the value of μ for 56° C. is 0·1055.

Plotting $\log y$ and $\log n$ as the coordinates of points on squared paper gives points which may be said to lie on two straight lines, but the errors of observation are too great. For $n>24$ we might perhaps say that $y \propto n^{1{\cdot}28}$; but it seems hardly fair to draw conclusions from this set of observations.

TABLE VIII.—March 24th, 1892. ($l=7{\cdot}025$ centim.)

$\theta°$ C.	n.	D.	y.	μ.
30	100	363	45·24	
30·8	78	250	31·79	
31	115	404	51·64	
31	32	62	7·92	·1903
31	22	47	6·01	·2103
31	17	37	4·73	·214
32	13	29	3·80	·2249
31	11	23·5	3·00	·2097
30	9·2	20	2·50	·209

y is $D/(l+\lambda)$ corrected to 31° C. by a correction of $2\frac{1}{2}$ per cent. per degree. The numbers of the last column have no meaning for speeds higher than n about $=32$. The average value of μ is 0·210. According to (9) the value of μ for 31° C. is 0·216.

Below $n=32$, $y \propto n$. Above $n=32$, we may perhaps say that $y \propto n^{1{\cdot}4}$.

TABLE IX.—March 28th, 1892. ($l=6{\cdot}525$ centim.)

$\theta°$ C.	n.	D.	y.
81	38·5	38	5·18
80·5	56	63	8·557
80	69	88	11·80
79·5	84	112	14·70
—	104	134	18·29
83	92	116	16·157

y means $D/(l+\lambda)$ corrected to 81° C.
The law seems to be $y \propto n^{1\cdot3}$ nearly.

TABLE X.—March 23rd, 1892. ($l=7{\cdot}025$ centim.)

$\theta°$ C.	n.	D.	y.
82	17·5	16	2·06
82	14	11	1·23
82	26	26	3·35
81	32	33	4·22
80	11·5	8·5	1·08
82	10	6·5	0·84

If it is assumed that $n=10$ is not much above the critical speed, μ may be calculated as 0·0646. According to (9) $\mu=0{\cdot}062$ for 81° C.

$y \propto n^{1\cdot30}$ may be taken as the law.

TABLE XI.—March 24th, 1892. ($l=6{\cdot}7$ centim.)

$\theta°$ C.	n.	D.	y.	μ.
65	9	8	1·07	·091
66	10·8	9	1·21	·086
65·5	17	16	2·14	·097
64·5	21	21	2·79	
65	23·5	26	3·46	
65	29	32	4·26	
65	114	210	28·00	
66	102	162	21·82	
64·5	88	156	20·10	
65	66	112	14·93	
66	52	74	9·96	
66	44·5	59	7·94	
66	38	46	6·19	

y is $D/(l+\lambda)$ corrected to 65° C. μ has no meaning except for the first three speeds, and the mean of these three is 0·091. According to (9) the value of μ for 65° C. is 0·085.

Above the critical speed, which is possibly below $n=17$, the law is probably $y \propto n^{1\cdot32}$.

It is not worth while to publish any of the observations which we have made upon other liquids, nor to publish the curves we have drawn for sperm-oil, although we exhibit them before the Society. Errors of one degree in observing temperature were quite possible, and errors of half a degree in the deflexion of our pointer were also possible. Small fluctuations in speed were continually taking place, so that the pointer was never quite still, the motion of the fluid was therefore not truly steady. It is our determination to repeat the whole work with improved apparatus. In the meantime, however, it will be observed from Table III. that there is fair agreement in the law connecting μ with temperature, from all the sets of observations. There is, on the whole, a very fair agreement with what we venture to call Prof. Reynolds's rule,

$$y=a\mathrm{F}^{2-\kappa}n^{\kappa},$$

where κ has the value 1·33 or 1 according as n is above or below the critical speed*. The sheet of squared paper on which we have plotted all our values of $\log y$ and $\log n$ for the various constant temperatures shows that the errors of observation are too great for the establishment of this value of κ; but it is the probable value. It shows, however, in the allineation of the points of discontinuity, with sufficient accuracy that $y_c \propto n_c^2$, if the rule is taken to be generally true; and although there is some little vagueness always in one's observations just about the critical speed, we may take $y_c=0\cdot009\,n_c^2$ without very great error. Indeed, we are satisfied with the substantial agreement of all our observations with the formula

$$y=a\left(\frac{\mu}{\cdot769\,a}\right)^{2-\kappa}n^{\kappa},$$

* Prof. Reynolds, in criticizing a proof of this paper, has been kind enough to point out that his rule for pipes does not necessarily apply to the fluid in our apparatus. We had not seen the reprint of his Royal Institution lecture, else we should have known that the condition of the liquid in circular flow is inherently stable or unstable according as r is greater or less than the radius of the fixed cylindric surface. As he points out, the liquid in the outer space is inherently stable for velocities far exceeding the critical velocity (if there is one) for plane surfaces, whereas the liquid in the inner space is unstable from the first.

We directed the attention of the meeting to the fact that Tables IV., V., VI., and VIII. give unmistakable evidence of the truth of what we have called Prof. Reynolds's Rule, however difficult we may find it in explanation.

where $a = \cdot 009$ and $\kappa = 1\cdot 33$. That is, for low speeds we have the law

$$y = \frac{\mu}{\cdot 769} n.$$

At the critical speed the law suddenly changes to

$$y = a\left(\frac{\mu}{\cdot 769\, a}\right)^{\frac{2}{3}} n'^{\frac{4}{3}},$$

which holds for all higher speeds which we have tried. The critical speed

$$n_c = \frac{\mu}{\cdot 769\, a} = 144\,\mu,$$

and

$$y_c = a n_c^2, \text{ or } \cdot 009\, n_c^2.$$

It is to be recollected that ρ is too nearly constant for us to say with certainty that a is proportional to ρ, as the theory requires. The errors of observation were so great that it was not worth while finding accurately the most probable values of κ and a.

We wish it to be understood that our apparatus was very carefully constructed, and great care was taken in making the observations; but it is our intention to pursue the investigation with apparatus much more carefully constructed.

Vibratory Experiments.

In designing the apparatus it was our intention to obtain μ from the damping of the rotational oscillations of the suspended cylinder about its vertical axis, the trough being at rest. We meant in this way to obtain μ for velocities very much smaller than those which could be employed in our steady motion experiments. A considerable number of observations were made, but when we tried to make calculations of μ we found that our mathematical difficulties were too great, and after many months of effort we are forced to say that we are unable to utilize these observations. In equation (4) assume that $v = w\epsilon^{ikt}$, and w may be obtained in Bessel functions. Unfortunately, as there are two surface conditions, *both* particular solutions of the Bessel equation are necessary, and the work of reduction becomes very great. An approximate solution is obtained by taking $r = \mathrm{R} + x$, R being the radius of the suspended cylinder, and taking the equation (4) to be

$$\frac{d^2v}{dx^2} + \frac{1}{\mathrm{R}}\frac{dv}{dx} - \frac{v}{\mathrm{R}^2} = \frac{\rho}{\mu}\frac{dv}{dt}. \quad . \quad . \quad . \quad (11)$$

Making this assumption in the case of steady motion, it was found that it was sufficiently correct for practical purposes.

The following numbers show the sort of error introduced, taking R=10, and 1 the greatest value of x.

Values of x.	Values of v.		
	Correct.	Approximate.	On the assumption of motion in plane layers.
0	1	1	1
·2	·7914	·7914	·8
·5	·4875	·4872	·5
·7	·2895	·2892	·3
1·0	0	0	0

The solution of (11) for vibratory motion is easy enough; but we found it still difficult to calculate μ from our observations. Even when we assume that the motion is in plane layers, so that the solution used by Maxwell is employed, we find that our $\frac{\mu}{\rho}$ is too great for a logarithmic decrement to exist with such amplitudes and times of oscillation as we had employed in the experiments, and it was impossible for us to repeat the experiments under the same conditions again at slower velocities, because the apparatus had been taken to pieces and could not be fitted up again in exactly the same way. When we say that a logarithmic decrement did not exist, we mean that it was not constant, but varied with the amount of the oscillation. For the tractive force to be proportional to the velocity of the cylinder it is necessary for μ/ρ and the periodic time to be so great that the velocities of the fluid at all places shall be in the same proportion as if the motion were steady.

After this paper was written we asked Mr. J. B. Knight, of the Chemical Department of the Finsbury Technical College, to make measurements of the specific gravity of sperm-oil at different temperatures. His results give a very striking confirmation of the views expressed in the paper as to a discontinuity of some kind due to rise of temperature. As all the authorities whom we have consulted seemed to see no possible reason for a discontinuity in the rate of change of μ with temperature in sperm-oil at about 40° C., it is possible that these results may be of importance.

Temperature Cent.	Specific Gravity.
25°	·831
30	·8306
35	·828
40	·826
45	·8758
50	·8753
55	·8717

We are now arranging a piece of apparatus which will give, not the absolute value of the specific gravity, but with great accuracy relative rates of the change of specific gravity with temperature *. We shall make experiments of the same kind upon other animal oils.

XLIV. *Note on the Effect of the Replacement of Oxygen by Sulphur on the Boiling- and Melting-points of Compounds.* *By* Miss A. G. Earp †.

In various papers published in the Philosophical Magazine ‡ Carnelley has called attention to the effect produced on the boiling-point and melting-point of compounds by replacing one element in the compound by another belonging to the same group. He gives numerous examples (mostly organic compounds) to show that in the case of the halogen compounds, when one halogen is replaced by another of a higher atomic weight, both the boiling- and melting-point are correspondingly raised.

As a further instance of the same kind of thing he gives the following series of the ethyl carbonates and sulpho-carbonates to show that the boiling-point is raised in proportion to the amount of sulphur introduced in the place of oxygen. He also points out that the same series shows that a definite effect is produced by a change in the arrangement of the molecule without any change in the number of sulphur atoms.

$CO\langle^{O-C_2H_5}_{O-C_2H_5}$	B.P. 125°.	$CO\langle^{SC_2H_5}_{SC_2H_5}$	B.P. 196°.
$CO\langle^{O-C_2H_5}_{S-C_2H_5}$	B.P. 156°.	$CS\langle^{OC_2H_5}_{SC_2H_5}$	B.P. 200°.
$CS\langle^{O-C_2H_5}_{O-C_2H_5}$	B.P. 161°.	$CS\langle^{SC_2H_5}_{SC_2H_5}$	B.P. 240°.

* We described at the Meeting results obtained for other specimens of sperm-oil, with the new apparatus, which exhibited no discontinuity. Yet we can find no reason to doubt Mr. Knight's measurements.

† Communicated by M. M. Pattison Muir.

‡ Phil. Mag. Oct. 1879.

He does not, however, mention the way in which this effect is reversed in the cases in which the oxygen of the *hydroxyl* group is replaced by sulphur, and I therefore conclude that it escaped his notice. By examining the large number of boiling-point data given by him in his tables I have found the following rule to be perfectly general :—

The replacement of oxygen by sulphur in a compound always raises *the boiling-point except in those cases in which the oxygen of the* hydroxyl *group is replaced by sulphur, and then the reverse effect is very marked.*

In obtaining data in proof of this I have been confined of course mainly to organic compounds, and of these I have only given the simpler instances, and such of the more complicated compounds as have a known structural formula. The reason for this is obvious, since Kopp has shown that the boiling-point of isomeric hydrocarbons is not the same, showing that a mere rearrangement of the atoms in a molecule is sufficient to affect the boiling-point without any change in number or kind. The fact is further exemplified in the series of ethyl-carbonates given above.

In the following list of compounds containing hydroxyl and their sulphur analogues, it will be seen that the replacement of the OH by the SH group always *lowers* the boiling-point, and that in the case of bodies of low molecular weight the difference is considerable, but decreases as we ascend a homologous series*.

	°		°	Diff. °
H_2S	−61·8	H_2O	100	161·8
CH_3SH	21	CH_3OH	67	46
C_2H_5SH	36·2	C_2H_5OH	78·4	42
$(CH_2SH)_2$	146	$(CH_2OH)_2$	197	51
CH_2CHCH_2SH	90	CH_2CHCH_2OH	96	6
$CH_3CH_2CH_2SH$	67	$CH_3CH_2CH_2OH$	97	30
$(CH_3)_2CHSH$	57	$(CH_3)_2CHOH$	83	26
$(CH_3)_2CHCH_2SH$	88	$(CH_3)_2CHCH_2OH$	108	20
$CH_3CH_2CHSHCH_3$	84	$CH_3CH_2CHOHCH_3$	99	15
$CH(CH_3)_2CH_2CH_2SH$	120	$CH(CH_3)_2CH_2CH_2OH$	131·5	11·5
$CCl_3CHOHSH$	123	$CCl_3CHOHOH$	149	26
C_6H_5SH	172	C_6H_5OH	180	8
$C_6H_4(SH)_2$	243	$C_6H_4(OH)_2$	270	27
$CH_3(CH_2)_4CH_2SH$	145	$CH_3(CH_2)_4CH_2OH$	157	12
$C_6H_5CH_2SH$	194	$C_6H_5CH_2OH$	205	11
$C_6H_4CH_3SH$ (α)	188	$C_6H_4CH_3OH$ (α)	188	0
„ (β)	188	„ (β)	201	13
„ (γ)	188	„ (γ)	198	10
CH_3COSH	93	CH_3COOH	117	24
C_6H_4OHSH (α)	216	C_6H_4OHOH (α)	245	29
† Exception :—$C_{10}H_7SH$(α)	285	$C_{10}H_7(OH)$(α)	278–80	

* The only exception to the rule is that marked †, and is in the case of a body of high molecular weight and complicated constitution.

Again, in the following list of compounds containing oxygen *not* in the condition of hydroxyl, it will be seen that the normal rule is followed.

	°		°	Diff. °
CH_3CHS	205	CH_3CHO	21	184
$(CH_2)_2S$	200	$(CH_2)_2O$	13·8	187
$(CH_3)_2S$	41	$(CH_3)_2O$	−23	64
$(CH_3)_2CS_3$	200	$(CH_3)_2CO_3$	91	109
$(C_2H_5)(CH_3)S$	64	$(C_2H_5)(CH_3)O$	11	53
$(C_2H_5)_2S$	92	$(C_2H_5)_2O$	35	57
$CH(CH_3)_2CH_2CHS$	114	$CH(CH_3)_2CH_2CHO$	85	29
$(C_2H_5)_2CS_3$	240	$(C_2H_5)_2CO_3$	125	115
$EtSCH_2SEt$	184	$EtOCH_2OEt$	88	96
$(CH_2CHCH_2)_2S$	140	$(CH_2CHCH_2)_2O$	82	58
$(CH_2CHCH_2)_2S_3$	188	$(CH_2CHCH_2)_2O_3$	171	17
$(Pr)_2S$ (α)	130	$(Pr)_2O$ (α)	82	48
,, (β)	120	,, (β)	60	60
$(EtSCH_2)_2$	210	$(EtOCH_2)_2$	123	87
$C_6H_5SC_2H_5$	204	$C_6H_5OC_2H_5$	172	32
$(CH_3CH_2CH_2CH_2)_2S$	182	$(CH_3CH_2CH_2CH_2)_2O$	140	42
$C_6H_5CH_2SEt$	215	$C_6H_5CH_2OEt$	185	30
$(C_5H_{11})_2S$(Iso)	250	$(C_5H_{11})_2O$ (Iso)	175	75
$(C_6H_4)_2S$	332	$(C_6H_4)_2O$	278–288	54–44
$(C_6H_5)_2S$	292	$(C_6H_5)_2O$	246	46
CH_3COSCH_3	95	CH_3COOCH_3	56	39
$CO(SCH_3)_2$	169	$CO(OCH_3)_2$	90	79
$CH_3COSC_2H_5$	115	$CH_3COOC_2H_5$	77	38
$CH_3COSC_3H_7$ (α)	135	$CH_3COOC_3H_7$ (α)	102	33
,, (β)	124	,, (β)	91	33
C_6H_4COOCS	284	C_6H_4COOCO	276	8
$C_6H_5COSC_2H_5$	242	$C_6H_5COOC_2H_5$	212	30
CH_3SCN	132	CH_3OCN	90	42
CH_3NCS	119	CH_3NCO	44	75
CH_3CHCH_2NCS	150	CH_3CHCH_2NCO	82	68
C_3H_7SCN (β)	151	C_3H_7OCN (β)	67	84
$CH(CH_3)_2CH_2NCS$	162	$CH(CH_3)_2CH_2NCO$	110	52
C_6H_4COSCO	284	C_6H_4COOCO	276	8
C_6H_5NCS	218	C_6H_5NCO	163	55
$C_6H_5CH_2NCS$	243	$C_6H_5CH_2NCO$	175–200	43
CCl_3SCCl_3	156–160	CCl_3OCCl_3	(about) 100	

To the above may be added the series of ethyl carbonates quoted at first, and also the following inorganic compounds:—

	°		°
CS_2	42·6	CO_2	−78·2
$CSCl_2$	71	$COCl_2$	82
$PSCl_3$	125	$POCl_3$	197

By arranging the data rather differently it is easy to see that the abnormality lies entirely with the hydroxyl group. Thus, if we take any group of sulphur compounds of one type, we shall find the boiling-point increases with the molecular weight as well when the hydrogen of the SH group is replaced by a hydrocarbon radical as in any other case.

Such, for example, are the following :—

	H_2S	$-61^\circ\cdot8$		H_2S	$-61^\circ\cdot8$		H_2S	$-61^\circ\cdot8$
	CH_3SH	21		C_2H_5SH	36		C_6H_5SH	172
A_1	$(CH_3)_2S$	41	A_2	$(C_2H_5)_2S$	92	A_3	$C_6H_5SC_2H_5$	204
	$C_2H_5 . CH_3S$	64		Pr_2S (α)	130		$(C_6H_5)_2S$	292

Taking in the same way the corresponding oxygen compounds, we find that by replacing OH by OX, where X stands for any *hydrocarbon radical*, unless *very* complex, we *lower* the boiling-point of the compound considerably, whereas when the exchange is simply between *different hydrocarbon* radicals the change is in the normal direction.

	H_2O	100°		H_2O	100°		H_2O	100°
	CH_3OH	67		C_2H_5OH	78·4		$(C_6H_5OH$	180
B_1	$(CH_3)_2O$	-23	B_2	$(C_2H_5)_2O$	35	B_3	$C_6H_5OC_2H_5$	172
	$CH_3C_2H_5O$	11		$(Pr_2)O$ (α)	82		$(C_6H_5)_2O$	246*

From these data it is evident that the fact that water, which has a lower molecular weight than even any of the "permanent" gases (except hydrogen) will remain liquid up to a very high temperature, is only one particular and well-marked case of the general effect of the hydroxyl group.

It has been objected by Ostwald and others that the comparison of boiling-points is unsatisfactory, inasmuch as in some cases it is possible that the vapour-pressure curves of different substances may *cross* one another at some point; and in that case, if some other than atmospheric pressure were taken as the standard, the relative position of the boiling-points would be reversed.

It is difficult to plot the vapour-pressure curves for H_2O and H_2S on the same scale, since the pressure of H_2S varies by many atmospheres ; while that of H_2O varies through the same range only by a few inches, so that it has to be represented on the H_2S scale by a line following the zero. The H_2S curve is, however, perfectly normal, and shows no tendency whatever to approach the zero at any point short of infinity. Hence the objection about the crossing of the curves falls to the ground in this case. The same may be shown by comparing the curves for CO_2 and CS_2; only in this case, of course, the sulphur compound follows the zero line, while the other is highly inclined.

With regard to the melting-points of oxygen and sulphur compounds the same general rule holds ; but exceptions are not rare, particularly in the cases of more complicated compounds, and naturally it is among these that the larger number

* In this case the destruction of OH is not sufficient to balance the effect of introducing the second carbon ring.

of melting-point data are given. In all probability the tendency to form molecular groupings and other unknown factors tend to obscure the effect on melting-points due to the change of constitution alone.

Another point which I think may be noticed with advantage from the series just given on page 461, and which, as far as I am aware, has been hitherto neglected, is the effect on the boiling-point of the *symmetry* of the molecule, unsymmetrical molecules tending to boil higher than symmetrical ones.

Consider the series A_1, page 461. Between the first and second members of the series there is a large difference, the molecular weight being increased and the symmetry of the molecule destroyed at the same time. Between 2 and 3 of the same series, on the other hand, there is a much smaller difference; the molecular weight is increased but symmetry is restored, and the two things act against one another.

Again, consider the series B_1. Between 1 and 2 in this series the destruction of hydroxyl *lowers* the boiling-point, the destruction of molecular symmetry tends to raise it, the result being that the *difference* only of the two effects is small. Between 2 and 3 the destruction of hydroxyl and the restoration of symmetry act together, and the resultant effect is large.

The same effects may be noticed by comparing A_2 and B_2 in the same way, and also by comparing the first, second, and fourth members in the series A_3 and B_3 respectively.

XLV. *Notices respecting New Books.*

An Elementary Treatise on Modern Pure Geometry. *By* R. Lachlan. (London: Macmillan. 1893. Pp. x+288.)

MR. LACHLAN is a recognized master of the Geometrical craft, and the work before us well maintains his reputation. His primary object is to meet the new Cambridge Tripos regulations, in which provision is made for the introduction of a paper on "Pure Geometry." All that could fairly be looked for in such a paper is given by the writer, or is led up to by him. He has not, however, contented himself with such a limited supply as this would require, but he has written with a view to allure students on to the arcana of the science. After a careful perusal we have detected very few errata. On page 53, Ex. 4 is obviously a slip, and in line 3 from bottom for Bx read By, for Cx read Cz. Page 55 line 13 contains a small clerical error: the opening

sentence of § 116 is not sufficiently guarded to be accurate. In Ex. 3, page 70, it is not stated what point S′ is. On page 161 line 11, for "polar" read "poles." Two or three clerical errors are easily corrected. The following historical one occurs on page 78, Ex. 6: "Mr. H. M. Taylor's paper was read before the London Mathematical Society on Feb. 14th, 1884," whereas he had previously published his Note, "On a six-point circle connected with a triangle," in the 'Messenger of Mathematics,' vol. xi. (May 1881–April 1882). If we mistake not, the "circle" had previously been given by him in a Trinity paper. In conclusion we are glad to say that the text is not overburdened with corollaries and superfluous matter, the figures are excellent, and there is a most judicious and varied selection of exercises.

Revue Semestrielle des Publications Mathématiques rédigée sous les auspices de la Société Mathématique d'Amsterdam. Tome I., 1re partie. (Amsterdam. 1893. 104 pp.)

THE object which the Mathematical Society of Amsterdam has in view in putting forth this *Revue* is "de faciliter l'étude des sciences mathématiques en faisant connaître, sans délai de quelque importance, le titre et le contenu principal des mémoires mathématiques publiés dans les principaux journaux scientifiques." Primarily it is intended for the use of its own Members, but the Society has rightly judged that such a publication, if well conducted, will be of service to a much larger circle of readers. This opening number contains titles of papers printed in about 120 journals, 19 of which are British and 8 American. A careful list of the titles is drawn up with various particulars of interest (pp. 87–104).

The title of each communication is preceded by a system of notation adopted at the recent Congrès International de Bibliographie des Sciences Mathématiques, and is followed by a very concise *Compte-rendu* of the contents. We may say that the *Revue*, though its objects are similar to those of the well-known *Fortschritte der Mathematik* (Berlin), does not aim so high, for in the generality of instances the insight into any paper given by the notices here is little more than a student would infer from the bare title. Its merit is that a much earlier record, if the editors keep up to date, will be available for authors and readers. The papers tabulated from this Journal are comprised in Vol. xxxiv. (Nos. 206–209) and are seven in number. Two are given by the titles only: of the others a fair abstract is given. Lord Rayleigh's papers are assigned to "J. W. S. Rayleigh." We wish the Society good success and a large *clientèle*.

XLVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 313.]

January 25th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

THE following communications were read :—

1. "On Inclusions of Tertiary Granite in the Gabbro of the Cuilin Hills, Skye; and on the Products resulting from the Partial Fusion of the Acid by the Basic Rock." By Prof. J. W. Judd, F.R.S., V.P.G.S.

The author first calls attention to previous literature bearing on the subject of the extreme metamorphism of fragments of one igneous rock which have been caught up and enveloped in the products of a later eruption. The observations of Fischer, Lehmann, Phillips, Werveke, Sandberger, Lacroix, Hussak, Graeff, Bonney, Sauer, and others show that, while the porphyritic crystals of such altered rocks exhibit characteristic modifications, the fused groundmass may have developed in it striking spherulitic structures.

On the north-east side of Loch Coruiskh, in Skye, there may be seen on a ridge known as Druim-an-Eidhne, which rises to a little over 1000 feet above the sea, a very interesting junction of the granitic rocks of the Red Mountains with the gabbros of the Cuilin Hills. At this place, inclusions of the granitic rock, sometimes having an area of several square yards, are found to be completely enveloped in the mass of the gabbro. The basic rock here exhibits all its ordinary characters, being a gabbro passing into a norite, traversed by numerous segregation-veins; the acid rock is an augite-granite, exhibiting the micropegmatitic ('granophyric') and the drusy ('miarolitic') structures, and it passes in places into an ordinary quartz-felsite ('quartz-porphyry').

Within the inclusions, however, the acid rock is seen to have undergone great alteration from partial fusion, and it has acquired the compact texture and splintery fracture of a rhyolite; weathered surfaces of this rock are found to exhibit the most remarkable banded and spherulitic structures.

Microscopic study of the rock of these inclusions shows that the phenocrysts of quartz and felspar remain intact, but exhibit all the well-known effects of the action of a molten glassy magma upon them. The pyroxene, however, has been more profoundly affected, and has broken up into magnetite and other secondary minerals. The micropegmatitic groundmass, which was the last portion of the rock to consolidate, has for the most part been completely fused, and in some places has actually flowed. In the glassy mass thus formed, the most beautiful spherulitic growths have been developed, the individual spherulites varying in size from a pin's head to a small orange. These spherulites are often

composite in character, consisting of minute examples of the common type enclosed in larger arborescent growths ('porous-spherulites') of felspar microlites, with silica, originally in the form of opal and tridymite, but now converted into quartz, lying between them. All the interesting forms of spherulitic growth which have been so well described by Mr. Iddings from the Obsidian Cliff in the Yellowstone Park, and by Mr. Whitman Cross from the Silver Cliff, Colorado, are most admirably illustrated in these inclusions of the Cuilin Hills. It is interesting to note that the nuclei of some of these large spherulites consist of fragments of the micropegmatitic granite which have escaped fusion. Among the new minerals developed in these inclusions, by the action on them of the enveloping magma, are pyrites and fayalite (the iron-olivine).

The phenomena now described are of interest as setting at rest all doubts as to the order of eruption of the several igneous masses of the Western Isles of Scotland. That the gabbros are younger than the granites was maintained by Macculloch in 1819, by J. D. Forbes in 1846, by Zirkel in 1871, and by the author in 1874. In 1888, however, Sir A. Geikie asserted that these conclusions were erroneous; he insisted that the granites were erupted *after* the gabbros and basalts, and that they are, indeed, later than all the volcanic rocks of the district except a few basic dykes which are seen to traverse them. The occurrence of the remarkable inclusions of granite within the gabbro now removes all possibility of doubt on the subject, and proves conclusively that the granite was not only erupted but had consolidated in its present form before the outburst through it of the gabbro.

2. "Anthracite and Bituminous Coal-beds. An Attempt to throw some light upon the manner in which Anthracite was formed; or Contributions towards the Controversy regarding the Formation of Anthracite." By W. S. Gresley, Esq., F.G.S.

The author does not seek to advance any new theory in this communication, nor to proclaim new facts of any importance, but to put old facts in something of a new light, in order to aid the investigations of others. His main object is to establish two facts, viz.:—that the associated strata of anthracite-beds are more arenaceous than those containing so-called bituminous coal-beds, and that the prevailing colours of the sandstones, grits, etc., of anthracite regions are greyer and darker than those of regions of bituminous coal. To these facts may perhaps be added a third, that the more anthracitic the coal-beds, and the more siliceous the enclosing strata, the harder and tougher these associated strata are.

While recognizing that the rocks of many anthracite regions have undergone great disturbance, he cites other areas where coal-basins have been much folded, without any corresponding production of anthracite in considerable quantity.

The modes of occurrence of anthracite are illustrated by many instances observed by the author in the Old and New Worlds.

February 8th.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read :—

1. "Notes on some Coast-Sections at the Lizard." By Howard Fox, Esq., F.G.S., and J. J. H. Teall, Esq., M.A., F.R.S., F.G.S.

In the first part of the paper the authors describe a small portion of the west coast near Ogo Dour, where hornblende-schist and serpentine are exposed. As a result of the detailed mapping of the sloping face of the cliff, coupled with a microscopic examination of the rocks, they have arrived at the conclusion that the serpentine is part and parcel of the foliated series to which the hornblende-schists belong, and that the apparent evidences of intrusion of serpentine into schist in that district are consequences of the folding and faulting to which the rocks have been subjected since the banding was produced. The interlamination of serpentine and schist is described, and also the effects of folding and faulting. Basic dykes, cutting both serpentine and schists, are clearly represented in the portion of the coast which has been mapped, and these locally pass into hornblende-schists, which can, however, be clearly distinguished from the schists of the country. The origin of the foliation in the dykes is discussed.

The second part of the paper deals with a small portion of the coast east of the Lion Rock, Kynance. Here a small portion of the 'granulitic series' is seen in juxtaposition with serpentine. The phenomena appear to indicate that the granulitic complex was intruded into the serpentine; but they may possibly be due to the fact that the two sets of rocks have been folded together while the granulitic complex was in a plastic condition, or to the intrusion of the serpentine into the complex while the latter was plastic.

2. "On a Radiolarian Chert from Mullion Island." By Howard Fox, Esq., F.G.S., and J. J. H. Teall, Esq., M.A., F.R.S., F.G S.

The main mass of Mullion Island is composed of a fine-grained 'greenstone,' which shows a peculiar globular or ellipsoidal structure, due to the presence of numerous curvilinear joints. Flat surfaces of this rock, such as are exposed in many places at the base of the cliff, remind one somewhat of the appearance of a lava of the 'pahoehoe' type.

The stratified rocks, which form only a very small portion of the island, consist of cherts, shales, and limestone. They occur as thin strips or sheets, and sometimes as detached lenticles within the igneous mass. The chert occurs in bands varying from a quarter of an inch to several inches in thickness, and is of radiolarian origin. The radiolaria are often clearly recognizable on the weathered surfaces of some of the beds, and the reticulated nature of the test may be observed by simply placing a portion of the weathered surface under the microscope.

The authors describe the relations between the sedimentary and

igneous rocks, and suggest that the peculiar phenomena may be due either to the injection of igneous material between the layers of the stratified series near the surface of the sea-bed while deposition was going on, or possibly to the flow of a submarine lava.

The forms of the radiolaria observed in the deposit, and also their mode of preservation, are described in an Appendix by Dr. G. J. Hinde.

3. "Note on a Radiolarian Rock from Fannay Bay, Port Darwin, Australia." By G. J. Hinde, Ph.D., V.P.G.S.

4. "Notes on the Geology of the District west of Caermarthen." Compiled from the Notes of the late T. Roberts, Esq., M.A., F.G.S.

To the east of the district around Haverfordwest, formerly described by the author and another, an anticlinal is found extending towards Caermarthen. The lowest beds discovered in this anticline are the *Tetragraptus*-beds of Arenig age, which have not hitherto been detected south of the St. David's area. They have yielded eight forms of graptolite, which have been determined by Prof. Lapworth. The higher beds correspond with those previously noticed in the district to the west; they are, in ascending order: (1) Beds with 'tuning-fork' *Didymograpti*, (2) Llandeilo limestone, (3) *Dicranograptus*-shales, (4) Robeston Wathen and Sholeshook Limestones.

Details of the geographical distribution of these and of their lithological and palæontological characters are given in the paper.

February 22nd.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Microscopic Structure of the Wenlock Limestone, with Remarks on the Formation generally." By Edward Wethered, Esq., F.G.S., F.R.M.S.

2. "On the Affinities (1) of *Anthracoptera*, (2) of *Anthracomya*." By Dr. Wheelton Hind, B.S., F.G.S.

3. "Geological Remarks on certain Islands in the New Hebrides." By Lieut. G. C. Frederick, R.N.

As far as can be judged from the soundings obtained, the New Hebrides are probably situated on a bank lying from 350 to 400 fathoms below the surface of the ocean and running in a N.N.W. and S.S.E. direction, with a deep valley between it and New Caledonia. The only two soundings obtained between these two groups are 2375 and 2730 fathoms, the former within a short distance of the New Hebrides.

Of the islands, Tanna is volcanic—an active volcano, apparently consisting entirely of fragmental material, being situate on its eastern side. Efaté has some volcanic rock, but is chiefly of coral formation. It rises to a height of 2203 feet, and in some parts has a terraced appearance, the terraces denoting distinct periods of

upheaval. Coral was found to the height of 1500 feet above sea-level. To the north of Efaté are Nguna, Pele, and Mau, of volcanic origin, and no coral has been found on them above sea-level; whilst Moso, Protection, and Errataka, to the west of Efaté, are of coral formation and similar in character to the adjoining coast of Efaté. In the vicinity of the coral isles is very little coral-reef, especially when the shores are steep. Delicate live corals were brought up from depths of 28, 39, and 42 fathoms off Moso, 37 fathoms near Mau, and 40 fathoms off Mataso. Mataso is a volcanic island with a narrow fringing-reef. Makura (6 miles N. of Mataso) and Mai are also volcanic, with narrow fringing-reefs partly surrounding the former and entirely encircling the latter island. A short distance west of Mai is Cook's Reef, of atoll formation. The Shepherd Isles are all of volcanic formation, apparently recent, and no coral was found growing around their shores. Mallicolo Island is of volcanic and coral formation. At one place in this island coral was found at a height of about 500 feet above sea-level.

March 8th.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Occurrence of Boulders and Pebbles from the Glacial Drift in Gravels south of the Thames." By Horace W. Monckton, Esq., F.L.S., F.G.S.

North of the Thames near London, the Glacial Drift consists largely of gravel, which is characterized by an abundance of pebbles of red quartzite and boulders of quartz and igneous rock. With the exception of very rare boulders of quartz, the hill and valley-gravels of the greater part of Kent, Surrey, and Berkshire are entirely free from these materials. The author points out that the River Thames is not, however, the actual southern boundary of the distribution of these Glacial Drift pebbles and boulders, though the number of localities where they are found in gravels south of that river is few. The author describes or mentions several, of which the following are the most important:—Tilehurst, Reading, Sonning, Bisham at 351 feet above the sea, Maidenhead, Kingston, Wimbledon, and Dartford Heath.

2. "On the Plateau-Gravel south of Reading." By O. A. Shrubsole, Esq., F.G.S.

This paper contains observations on the gravel of the Easthampstead-Yately plateau.

The constituent elements of the gravel are described, and the author notes pebbles of non-local material near Cæsar's Camp, Easthampstead, on the Finchampstead Ridges, and at Gallows Tree Pit at the summit of the Chobham Ridges plateau. He mentions instances of stones from the gravel of the plateau (described in the paper) which may bear marks of human workmanship. He furthermore argues that the inclusion of pebbles of non-local origin

in the gravels may be due to submergence of the plateau up to a height of at least 400 feet above present sea-level, and cites other facts in support of this suggestion. He concludes that the precise age of the gravel can only be more or less of a guess, until the mode of its formation has been definitely ascertained.

3. "A Fossiliferous Pleistocene Deposit at Stone, on the Hampshire Coast." By Clement Reid, Esq., F.L.S., F.G.S.

This is practically a supplement to a paper, 'On the Pleistocene Deposits of the Sussex Coast,' that appeared in the last volume of the Quarterly Journal. An equivalent of the mud-deposit of Selsey has now been discovered about 20 miles farther west, and from it have been obtained elephant-remains, and some mollusca and plants like those found at Selsey. Among the plants is a South European maple.

XLVII. *Intelligence and Miscellaneous Articles.*

ON VILLARI'S CRITICAL POINT IN NICKEL.
BY PROF. HEYDWEILLER.

THE magnetism of iron, nickel, and cobalt changes under the influence of stretching forces. Villari first observed a special behaviour of iron in reference to this attribute, namely that with moderately strong magnetization small stretching forces increase the magnetism, while larger forces diminish it; thus the strength of the magnetism is graphically represented as a function of the load, the ordinates of the curve first increase up to a maximum and then diminish to far below the original values. The point of the curve at which the ordinate again reaches the original value is named Villari's critical point.

In nickel this property has not been observed up to the present; in this case, so far as hitherto known, the magnetism steadily decreases with increasing load. But with strongly magnetized soft iron also, with small load, the original increase of the magnetism vanishes, and it was thought probable that with sufficiently weak magnetization nickel also possesses a Villari's critical point. Experiments have confirmed this expectation. In observing the changes in the very feeble magnetizations, it was found necessary to work with a very sensitive arrangement.

A chemically pure nickel wire, 46 cm. long and 0·15 cm. thick, was suspended vertically with its lower end very near (3·5 cm. distant) the upper magnetic needle of an astatic system, and so that small longitudinal displacements caused no perceptible alteration in the direction of the needle. An intensity of magnetization $I=1$ C.G.S. unit corresponded to about 90 p throw with 110 p scale distance.

The reduction of the observed numbers to absolute measure was effected by comparison with an auxiliary magnetometer with single needle.

The observations were conducted with alternate loading and unloading, the strength of field remaining constant. The load never exceeded 1 kilog. per sq. mm. cross section of the wire.

With small strength of magnetization under 2 C.G.S. units and with the smallest loads, soft annealed nickel shows a small decrease of magnetism, with somewhat larger an increase, which may rise to 26 per cent. of the total magnetism, and finally again a decrease with increasing load.

Thus, for example, for the intensity of magnetization I=0·97 C.G.S. units with a load of p gr. per sq. millim. cross section, there were obtained the following respective variations of magnetization $\frac{\delta I}{I}$.

p.	$\delta I/I$.	p.	$\delta I/I$.
28	−0·006	347	+0·067
46	−0·011	490	+0·042
63	−0·014	738	+0·257
102	−0·019	904	+0·162
165	−0·029	977	+0·155
246	+0·015		

With stronger magnetization the increase becomes continually smaller; moreover after-effects of the preceding loading and phenomena of hysteresis show themselves to a considerable degree.

Hard-drawn nickel presents the same phenomena with much stronger magnetization still, even though in feebler degree.

Thus with a hard-drawn nickel wire, for I=55·5 C.G.S. units the variations of magnetization with a load of p gr. per sq. mm. were:—

p.	$\delta I/I$.	p.	$\delta I/I$.
9	−0·0034	84	+0·0187
18	−0·0052	113	+0·0180
27	−0·0054	246	+0·0122
33	−0·0062	360	+0·0080
42	+0·0081	490	−0·0304
56	+0·0186	740	−0·0682

We may therefore assert that, with reference to the above-discussed phenomena, the behaviour of nickel agrees well with that of iron quantitatively but not qualitatively.

The detailed communication of the method of experimenting and the results will be given in another place.—*Sitzb. Würz. Phys.-med. Ges.* March 11, 1893.

ON THE INTERFERENCE-BANDS OF GRATING-SPECTRA ON GELATINE. BY M. CROVA.

Photographed gratings applied on bichromated gelatine by M. Izarn's * method may give rise to straight or curved interference-bands, sometimes very irregular, in the spectra which they produce; similar bands have been produced by Brewster † in other circumstances. These phenomena are obtained with great beauty on the spectra obtained by reflexion on gelatine-gratings on silvered glass.

M. Izarn, in mentioning these interference-bands, expresses the opinion that they are connated with the interference phenomena by parallel gratings which I formerly investigated ‡.

Sunlight reflected from a heliostat is caught on a very narrow slit the image of which is projected upon a screen; a very small image of the sun is produced at the focus of this lens, which is received on the striated surface of a grating photographed on gelatine on silvered glass; the real images of the slit and of the diffracted spectra are received on a screen placed in the conjugate focus of the slit in respect of the lens.

The diffraction spectra are furrowed with large rectilinear black bands parallel to the rays, and which are almost absolute minima, the intensity of the rays reflected on the silvered surface being very little less than that of the rays which fall on the gelatine.

With a copy of a fine Brunner's grating, which I owe to the kindness of M. Izarn, the spectra of the first order present a large dark band in the green when the grating is very dry; if the surface is breathed on the band is displaced towards the violet; other and closer ones enter at the red end, and their number rises to three when the deposit of moisture confuses the projection. The same phenomena are produced but in the opposite direction during drying, and the displacement of the bands becomes very rapid if the evaporation is accelerated by blowing air over the grating.

If the incident light extends over the whole height of the grating instead of only to a small portion of the surface which is obtained by varying the distance from the lens, the fringes are curved, become irregular, and are sometimes serrated.

The phenomenon is due to the interference of two parallel gratings; the one real, situated at the surface of the gelatine in the points in which the incident wave meets its discontinuous part; the other virtual, which is its image in the silvered mirror. Their distance, which is virtually constant, is the optical path, $2\,ne$, e being the thickness, and n the index of the gelatine. At the focus of the lens, since the light only affects a small part of its surface, the thickness of the gelatine is virtually constant.

* *Comptes Rendus*, vol. cxvi. p. 506.
† Phil. Mag. [4] vol. xxxi. pp. 22 and 98 (1866).
‡ *Comptes Rendus*, vol. lxxii. p. 855, and vol. lxxiv. (1871–1873).

If, on the contrary, the light extends over a considerable surface, the thickness of the gelatine varies at different parts, especially if the plate has been placed vertically while drying; the bands are then bent while diverging, and their greatest divergence is at the part where the layer is thinnest.

When the grating has been prepared, the distortion of the bands is very irregular; but after a great number of hydratations followed by dryings the phenomenon becomes more regular. After fixing the grating in water and drying, the gelatine possesses, as is known, a kind of temper which is manifested by its accidental double refraction; but when it has been hydrated and dried slowly a great number of times its structure becomes more homogeneous, and the bands no longer possess serrations. It is possible that such alternations injure the good keeping of the gratings, and it is thus desirable to keep them in a dry place.

Observing the band-spectra in the goniometer they appear like broad and very dark spaces, but if sun-light is used condensed on the slit, by a cylindrical lens, the pivot lines of the spectrum are defined in these spaces with marvellous precision. The production of these parasitical bands does not affect the accuracy of measurements made with these gratings.

With gratings in gelatine on transparent glass these phenomena are scarcely perceptible by reflexion or by transmission, owing to the almost total identity of the refractive indices of gelatine and glass.

If the index of gelatine is taken at 1·52, it is easy to calculate the thickness of the layer of gelatine as a function of the number of bands contained in the spectrum reflected on silver; I have thus found that in the copy which I use the thickness of the layer is 0·04 millim. when it is dry, and about 0·16 millim. when it is at its maximum hydratation; this number is only approximate, as the index varies with the quantity of water it contains.

M. Izarn's gratings are of admirable sharpness, and examined in the microscope they do not differ from the original; in a Froment's grating, a hundred one, which I possess, the opaque interval is virtually equal to a fifth of the transparent interval: this is also the case with M. Izarn's copy; this is not a negative but a positive. The transparent intervals are the bands of insoluble gelatine, while the opaque intervals are the places where the soluble gelatine has been dissolved away by the water; but owing to the extreme fineness of the intervals, the water by capillary action has hollowed out cylindrical grooves which to a plane wave behave like an opaque body. When the opaque interval is very great compared with the transparent one, the opposite might take place; but it is easy to see that even when the two intervals are transparent, the difference of the refractive indices of gelatine and air is sufficient to produce phenomena identical with those of the grating. This question calls for new investigations.—*Comptes Rendus*, March 27, 1893.

THE

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PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

JUNE 1893.

XLVIII. *Electrochemical Effects due to Magnetization.* *By* GEORGE OWEN SQUIER, *Ph.D., Lieut. U.S. Army* *.

INTRODUCTION.

THE influence of magnetism on chemical action was the subject of experiment by numerous investigators during he first half of the present century †. Up to 1847 we find by no means a uniformity of statement in regard to this subject, and secondary effects were often interpreted as a true chemical influence. Among the earlier writers who maintained that such an influence exists may be mentioned Ritter, Schweigger, Döbereiner, Fresnel, and Ampère; while those of opposite view were Wartmann, Otto-Linné Erdmann, Berzelius, Robert Hunt, and the Chevalier Nobili.

Professor Remsen's discovery, in 1881, of the remarkable influence of magnetism on the deposition of copper from one of its solutions on an iron plate, again attracted attention to the subject, and since then considerable work has been done directly or indirectly bearing on the question.

Among other experiments by Professor Remsen ‡ were the action in the magnetic field of copper on zinc, silver on zinc, copper on tin, and silver on iron, in all of which cases the magnet evidently exerted some influence. With copper sulphate on an iron plate the effects were best exhibited, the

* Communicated by the Author.

† Wartmann, Philosophical Magazine, 1847, (3) xxx. p. 264.

‡ American Chemical Journal, vol. iii. p. 157, vol. vi. p. 430; 'Science,' vol. i. no. 2 (1883).

copper being deposited in lines approximating to the equipotential lines of the magnet, and the outlines of the pole being distinctly marked by the absence of deposit.

Messrs. Nichols and Franklin * were the next to conduct experiments bearing on this subject. They found that finely divided iron which has become "passive" through the action of strong nitric acid suddenly regains its activity when introduced in a magnetic field, and also that when one of the two electrodes immersed in any liquid capable of chemically acting upon them is placed in a magnetic field, a new difference of potential is developed between them due to this magnetization. They ascribe these effects to electric currents in the liquid produced indirectly by the magnet, which currents go in the liquid from the magnetized to the neutral electrode.

Professor Rowland and Dr. Louis Bell † were the first to note the "protective action" of points and ends of magnetic electrodes, and to give the exact mathematical theory of this action. Their results were *directly opposite* to those of Messrs. Nichols and Franklin, who found, as stated above, that points and ends of bars in a magnetic field acted like zincs to the other portions, or were more easily dissolved by the liquid.

The method of experiment adopted by Professor Rowland was to expose portions of bars of the magnetic metals placed in a magnetic field to reagents which would act upon them chemically, and study the changes in the electro-chemical nature of the exposed parts by fluctuations in a delicate galvanometer connected with the two bars. Iron, nickel, and cobalt were experimented upon, and nearly thirty reagents were examined in this manner. The results are summed up in the following statement :—"When the magnetic metals are exposed to chemical action in a magnetic field, such action is decreased or arrested at any points where the rate of variation of the square of the magnetic force tends towards a maximum."

Other investigations in this field are those of Andrews ‡, who employed iron and steel bars from eight to ten inches long with their ends immersed in various solutions, and one bar magnetized by means of a solenoid. The protective action was not noted, but, on the contrary, the magnetized

* American Journal of Science, vol. xxxi. p. 272, vol. xxxiv. p. 419, vol. xxxv. p. 290.

† Phil. Mag. vol. xxvi. p. 105.

‡ Proceedings of the Royal Society, no. 44, pp. 152-168, and no. 46, pp. 176-193.

bars acted as zincs to the neutral bars, thus indicating that they were more easily attacked.

Practically the same results were obtained by Dr. Theodor Gross * ; soft iron wires, 8 cm. long and 3 cm. in diameter, coated with sealing-wax except at the ends were exposed to various liquids. When one electrode was magnetized, a current was obtained going in the liquid from the magnetized electrode to the non-magnetized electrode.

It thus appears that there is at least an apparent inconsistency between the protective results of Professor Rowland and Professor Remsen, and those of Nichols, Andrews, Gross, and others, who find the more strongly magnetized parts of iron electrodes more easily attacked than the neutral parts; and it was with the object of endeavouring to reconcile these results, and of studying the *exact nature* of the influence exerted by the magnet, that the experiments recorded in this paper were undertaken.

Apparatus and Method of Investigation.

The method of investigation was that adopted by Professor Rowland in his previous work on the subject, since its facility and delicacy permitted the effects of the magnet to be observed whenever there was the slightest action on the electrodes by the solution examined, and the investigation could thus be carried over a wide range of material.

A large electromagnet was employed to furnish the magnetic field, and, at a distance sufficient to prevent any direct influence due to the magnet, a delicate galvanometer of the Rowland type was set up. Small cells were made with iron electrodes of special forms, coated with sealing-wax except at certain parts, and immersed in a liquid capable of acting chemically on iron. The whole was contained in a 50 cubic centim. glass beaker, and when joined to the connecting wires of the distant galvanometer was firmly clamped between the poles of the electromagnet.

In the course of the examination of a number of substances it was found necessary to use two galvanometers—one specially made by the University instrument-maker and very sensitive, which was employed with acids which evolve hydrogen; the other, much less sensitive, was best suited to the violent "throws" with nitric acid and iron. The samples of iron used throughout the experiments were obtained from

* "Ueber eine neue Entstehungsweise galvanischer Ströme durch Magnetismus," *Sitzungsberichte der Wiener Akademie*, 1885, vol. xcii. (1885) p. 1373.

Carnegie, Phipps, and Co., of Pittsburg, and were practically pure.

In order to insure a uniform density of surface, the electrodes were turned from the same piece and polished equally with fine emery-cloth. The magnet could be made or reversed at the galvanometer, and its strength varied at will by a non-inductive resistance. The electrochemical effects due to the magnetic field could thus be studied with facility by the fluctuations of the galvanometer-needle. The original difference of potential, which always existed between the electrodes, was compensated by a fraction of a Daniell cell, so the effects of a variation of the magnetic field could be observed when no original current was passing between the electrodes.

The standard cells were made with care, and under uniform treatment possessed at 20° C. an electromotive force of 1·105 volt. The connexions with the compensating circuit, which contained a finely-divided bridge, were so arranged that from its readings the difference of potential between the distant electrodes became known at once without involving the resistance of the cell or of the galvanometer.

Since quantitative measurements of the effects observed were desired, a preliminary step was to calibrate the electromagnet for a given distance apart of the pole-pieces. The method employed was the well-known one of comparing the galvanometer deflexions produced by a test-coil in the field with those of an earth inductor in series in the circuit. Since the effect of the sudden addition of a certain strength of field was wanted instead of its absolute value, the deflexions with the test-coil were taken for simple "make" or "break" and not for reversed field, thus eliminating the residual magnetism of the pole-pieces.

In the formula applicable, viz.,

$$\frac{\mathrm{H}}{\mathrm{H}'}\frac{\pi n a^2}{\pi n' a'^2}=\frac{d}{d'} \text{ nearly,}$$

in which d and d' represent the deflexions due to the inductor and test-coil respectively, H and H′ the earth's field and the field to be measured, n and n' the number of turns, and a and a' the radii of the coils, the particular values were :—

$$\pi n a^2 = 20716 \text{ square centim.}$$
$$\pi n' a'^2 = 6{\cdot}788 \text{ square centim.}$$
$$d = 4{\cdot}697.$$

Distance between pole-pieces 3·5 centim.

$H' = 1299{\cdot}48\ d'H$, and as d' varied from $\frac{1}{20}$ to 16, the range of field employed was from 65 to 20,800 H.

A curve was constructed so that from accurate ammeter readings in the field circuit the strength in absolute measure could be read off at once.

Experimental Results.

Preliminary.—The first experiments were made with very dilute nitric acid and iron electrodes—one a circular disk of 5 millim. radius, and the other a small wire 1 centim. long and 1 millim. in diameter, turned to a sharp point at one end. The point was placed opposite the centre of the disk, at a distance of 1 centim. from it, and the whole placed so that the cylindrical electrode coincided with the direction of the lines of force. When the minute point and the centre of the disk were exposed to the liquid, and the magnet excited, a momentary "throw" of the galvanometer was observed in the direction indicating the point as being protected or acting as the copper of the cell.

When the pointed pole was slightly flattened at the end, and the insulation so cut away that the surfaces of exposure on the two electrodes were exactly the same, the throw of the galvanometer on making the field was very much diminished, although still perceptible, since the disposition of lines of force would still be very different over the two plane surfaces of exposure.

With ball-and-point electrodes precisely similar phenomena were observed as with a disk and point, except to a less degree.

The gradual reversal of the current shortly after exciting the field, the independence of the throw of the direction of the current through the magnet, the disappearance of the throw when the nature of the magnetic field at the exposed parts became the same, and the effects of artificially stirring the liquid, were observed exactly as described by Messrs. Rowland and Bell.

In the course of a large number of preliminary experiments with nitric acid, it was soon observed that under certain conditions the effect of suddenly putting on the magnetic field was to produce a less rapid deflexion of the galvanometer in the *opposite* direction, or indicating the point as acting as a zinc. Plainly this irregular behaviour, due to the magnet, required a more systematic study than it had yet received. It had been found that the reversal of the current, which regularly followed the "protective throw," was decreased or destroyed by anything which prevented free

circulation in the liquid, and that an acidulated gelatine, which was allowed to harden around the poles, was best suited for this purpose. The great irregularity observed in any one experiment made it necessary to eliminate everything possible which might mask the true phenomenon, if any accurate comparisons were to be drawn between the effects observed in the different cases; accordingly a standard form of experiment was adopted, which was carefully repeated many times. The cell found best suited for this purpose was composed as follows :—

Disk electrode, diameter	14·4	millim.
„ „ thickness	2·6	„
Point electrode, total length	15·2	„
„ „ diameter	4·4	„
„ „ length of point	5·2	„
Distance of point from centre of disk	10	„

The same electrodes were used throughout any set of experiments, being carefully cleaned and polished each time.

With nitric acid the liquid was finally made up as follows :—

Distilled water	10 grammes.
Hard gelatine	1 gramme.
C. P. nitric acid (sp. gravity 1·415)	0·533 gramme.

The gelatine and water were allowed to stand until the former had dissolved without the application of heat, when the acid was added and the whole thoroughly mixed. Too strongly acidulated gelatine would not harden at all.

In some cases, in order to protect the point from the *beginning*, the electrodes, secured as usual at the ends of two small glass tubes containing the connecting wires, were firmly clamped in the proper position between the poles of the magnet, and the magnetic field put on before the cell was completed, by pushing the beaker containing the solution up in position round the electrodes.

With this cell a series of parallel experiments were conducted to obtain the variation of the effects with time, the amount of iron salts present, the fluidity of the solution, and with constant and variable magnetic fields.

A. *Behaviour of the Cell with Time, in the Earth's Field.*

The cell was placed entirely outside the magnetic field, and galvanometer-readings taken at intervals of one minute for three hours. The curve fig. 1 (I.) shows these results. Positive ordinates indicate a current from the point to the disk,

and negative ordinates the reverse current. Other experiments with fresh solutions, same electrodes, same exposed area, and every condition as nearly as possible the same, gave curves of practically the same character, and the one given is selected to illustrate.

The curve indicates that the original current was to the point electrode; this gradually decreased, owing to polarization, until after a hour and five minutes it reversed slightly, but again reversed thirty-five minutes later, and after a little more than two hours the deflexion became perfectly constant, remaining so indefinitely.

The iron salts formed could not move with facility from the exposed surfaces through the hardened gelatine, and were easily outlined from their brown colour, as the whole apparatus was placed in a strong light.

B. *In a Uniform Magnetic Field.*

The cell was next placed in the magnetic field, which was kept practically uniform (about 15,650 H) for three hours, and galvanometer-readings taken as before.

The electrodes were magnetized before being introduced into the solution, so as to protect the point from the beginning. In order to prevent the influence of the rise of temperature due to the heating of the field coils of the electromagnet, the whole cell was packed with cotton-wool between the poles. As Gross and Andrews observed, the temperature effect was small, the solution rising but 0°·7 C. in half an hour.

The curve fig. 1 (II.) shows the results of these observations. It is seen that the original current was, as before, to the point electrode, and about the same in value. This reversed after forty-five minutes, and rapidly increased to approximately twice its original value at the end of one hour and twenty minutes, and, instead of again reversing, remained indefinitely with the point electrode as a zinc. The distribution of the iron salts in this case was quite unlike the former. Notwithstanding the gelatine, the powerful magnetization of the exposed point gradually drew the iron salts from the disk as fast as they were formed, and concentrated them symmetrically about the point, giving the solution in this region an almost black appearance.

After waiting a sufficient time to be assured that further presence of iron salts would not effect the permanency of the existing electromotive force, the magnetic field was gradually decreased *without ever breaking circuit*, by increasing the

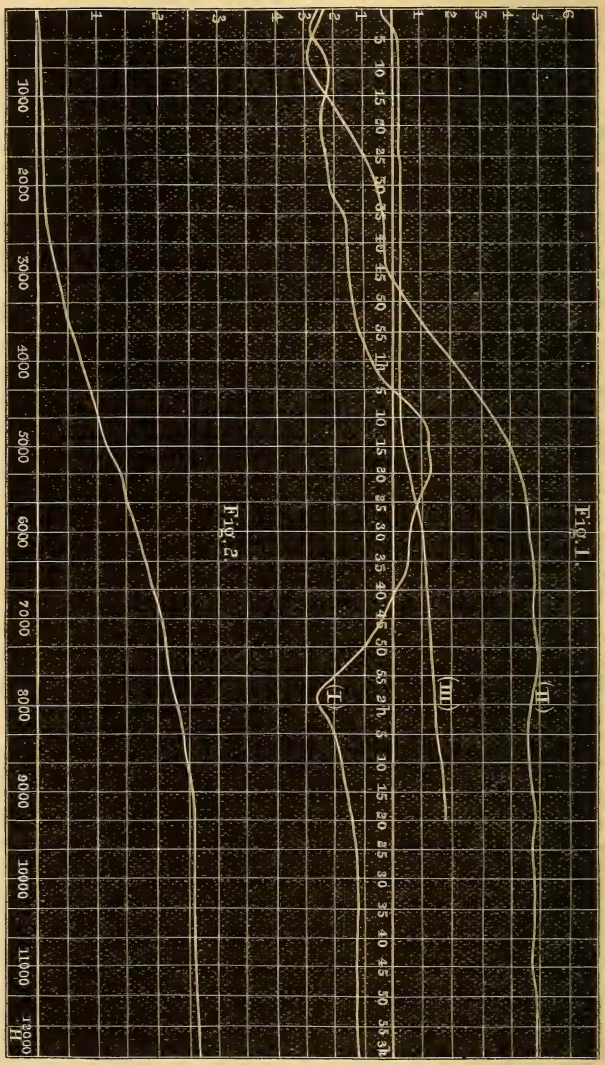


Fig. 1.
Fig. 2.
(I)
(II)
(III)
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
H

Fig. 3

liquid resistance in the field current. This change of resistance was necessarily made more or less suddenly, and the deflexion experienced at each increase of resistance a not very sudden throw toward reversal, in every respect the same as had been repeatedly observed in the preliminary experiments, and very different from the characteristic "protective throw," which is always sudden and in one direction.

By simply varying the field current with care, as explained above, the deflexion could be reversed again and again at will, and could also be held at the zero of the scale, indicating no current at all, as long as desired. When once the field was entirely broken, the iron salts were released from the control of the exposed pole, seriously disturbed by gravity, and putting on the field again failed to reproduce the results noted above.

The only elements of difference in the two cases are, (*a*) the magnetized condition of the metal, (*b*) the distribution of the iron salts formed by the reaction.

Although, as the curves indicate, the average electromotive force with the magnetic field was much greater than in the former case, yet this electromotive force is due to the difference of action at the two exposed surfaces, and, as will be pointed out later, the total amount of iron dissolved and passing into solution in the two cases is probably not very different *. Quantitative experiments are wanting on this point.

The influence of the magnetized condition of the metal and its magnitude is exhibited in the phenomenon of the "protective throw," which is always observed with apparatus sufficiently delicate unless it is masked by other secondary phenomena.

Since the electrodes were embedded in hardened gelatine, there could be no convection-currents in the liquid, and this can be eliminated. Evidently the great difference in the behaviour of the cell in the two experiments described is principally due, either directly or indirectly, to the distribution of the iron salts formed by the reaction in the two cases.

The principal *time* effects of the magnet were :—

(*a*) To produce a higher potential at the point of greater magnetization.

(*b*) To increase the rate of change of the potential between the electrodes and the absolute value of this potential difference.

(*c*) It also appears from both curves that after a certain distribution of iron salts is reached, further presence of the same does not affect the permanency of the current established.

* Fossati, *Bolletino dell'Elettricista*, 1890.

Since the time effects of the magnet were so marked, it was thought possible that a "cumulative" effect, due to the earth's field alone, might be detected after a sufficient time had elapsed. The apparatus was made as delicate as possible, and parallel experiments conducted, the electrodes first being placed in the magnetic meridian, and afterwards perpendicular thereto. No positive difference could be detected.

C. *Convection-Currents in the Liquid.*

As has already been stated, the reversal of the current which regularly followed the "protective throw" was found by Messrs. Rowland and Bell to wholly disappear when hardened acidulated gelatine was substituted for the dilute acid solution, so that when the magnet was put on a permanent deflexion of much less magnitude was obtained instead of a transitory throw. This indicated that currents in the liquid cannot be neglected, and their study was next undertaken. Since hardened gelatine completely prevented the reversal of the current, and with no gelatine it regularly appeared after a short time, a large number of experiments were made, in which the amount of gelatine was varied continuously between these limits. As expected, the effects also varied—the greater the fluidity of the solution, the more quickly the reversal occurred.

In the light of what was already known concerning the presence of iron salts, some of the experiments were continued over a considerable time, and in others iron salts were introduced artificially, to increase the effects. It was soon found that by starting with a fresh hardened gelatine, with which the "protective throw" was the only feature, and gradually increasing the fluidity of the solution and the amount of iron salts present, both effects were exhibited at the making of the field—first, the sudden throw of the needle always in the direction to protect the point, and immediately thereafter the comparatively slow "concentration throw" in the opposite direction. By making the conditions still more unfavourable for the "protective throw," it gradually diminished until entirely masked by the second effect, so that making the field produced a deflexion in the direction indicating a current from the point.

With the proper conditions, both of these effects could be studied with the greatest ease: first, one made prominent, then both equal, then the other made prominent at will. The "protective throw" could be traced until it became a mere

stationary tremor of the needle at the instant of its starting on the "concentration throw." This latter, though called a "throw," can be made to vary from an extremely slow continuous movement of the galvanometer deflexion, as in experiment B already described, to a comparatively rapid deflexion at the instant of making the magnet.

By using simply a dilute nitric-acid solution with no gelatine, and inserting a thick piece of glass between the electrodes, the concentration effect was delayed enough to allow the "protective throw" to first appear, with considerable iron salts in the solution; and on making the field both effects were observed as described above.

It now appears that the reversal of the current, uniformly observed in the experiments of Messrs. Rowland and Bell, was but a form of the "concentration throw" mentioned above, and that we can regard the substitution of the hardened acidulated gelatine for the dilute acid as merely separating these effects, so that the former can be studied by itself; in other words, the reversal of the current would have occurred just the same after a sufficient time had elapsed.

Turning to the experiments of Drs. Gross and Andrews, they employed but one magnetized electrode, which was not pointed. In this case the nature of the magnetic field at the two exposed surfaces would be very much more nearly the same than when a pointed electrode is employed. This arrangement is not, therefore, suited to bring out the delicate "protective throw," and it is not surprising that the concentration effect was the prominent feature observed.

We have now a complete reconciliation of the *directly opposite results* referred to in the introduction. The "protective throw" is due to the actual attraction of the magnet for the iron, and is always in the direction to protect the more strongly magnetized parts; while the "concentration throw" is always in the opposite direction, and depends upon the distribution of the iron salts present in the solution, and the convection-currents in the liquid. The concentration of the products of the reaction about the point would tend to produce a ferrous reaction instead of a ferric, and experiment shows that a higher electromotive force is obtained with cells in which a ferrous reaction takes place than with those in which a ferric reaction occurs; and this change in the *character of the reaction* produced by the concentration probably accounts, at least in part, for the increased electromotive force at the point.

D. *The Iron Salts about the Point Electrode.*

The effect of artificially stirring the liquid, and the direct influence of the fluid condition of the solution on the deflexions observed, at once suggested movements of the liquid, produced indirectly by the magnet. In order to locate these currents and determine their potence, a small cell was made of two rectangular pieces of glass held by stout rubber bands to thick rubber sides. Perforations in the sides admitted the electrodes, which were point and disk as before. The cell, between the poles of the electromagnet, was in a strong light, and the movements in the liquid were easily perceptible from the displacements of suspended particles introduced for the purpose. When very dilute nitric acid was placed in the cell and the magnet excited, some interesting phenomena were observed.

The liquid, at first colourless, almost immediately assumed a pale brown colour about the point, but nothing appeared at the disk electrode. The iron salts were drawn as soon as formed towards the point electrode, since here the rate of variation of the square of the magnetic force is a maximum.

As more iron was dissolved, a surface approximating to an equipotential surface of the pointed pole, and enveloping the coloured iron salts, was observed enclosing the point and at some distance from it. The outline of the surface became darker in a short time, and finally two or more dark contours, separated by lighter portions and symmetrical with the outer one, appeared between it and the point, indicating maxima and minima of density. When the magnetic field was gradually increased, this surface usually enlarged without breaking up and holding the iron salts within it. On further strengthening the magnetic field to about 16,000 H, the ridges merged into one thick black envelope around the point.

This phenomenon is best studied with but little iron salts present, and by watching the point electrode with a microscope while the strength of the magnetic field is increased and decreased continuously. The sections (fig. 3) show the general form of these contours with different strengths of field.

Upon breaking the field everything dropped from the point suddenly to the bottom of the cell, and on making the field again it required a few seconds for the salts to reappear at the point.

This, at least partially, accounted for the sudden effects often noticed at breaking the field circuit, and the compara-

tively small ones at "make," especially with certain salt-solutions, such as copper sulphate.

The outer envelope which held the iron salts together, and limited the immediate influence of the magnetized point, was distinctly defined within the liquid, and easily observed by the reflexion of the light from its convex surface.

The persistency with which the iron salts were held about the point was shown by moving the cell with respect to the electrodes, when the contour remained approximately intact, passing bodily through the liquid without being broken up.

E. *Electromagnetic Rotations.*

The small dust particles present in the liquid were drawn radially toward the point until they reached the surface described, when they pierced it and began to revolve rapidly about the point inside this surface, in the opposite direction to the currents of Ampère. Reversing the poles of the magnet produced surfaces of the same appearance but opposite rotations.

When the current from a Daniell cell was sent through it seemed to have very little effect upon the rotations, showing them to be controlled by the powerfully magnetized point.

The electromagnet was arranged with its field vertical, and the point electrode along the lines of force as before. This arrangement gave better control of the surfaces formed, since gravity now acted symmetrically about the point.

When a single iron rod about 3 millim. in diameter, and placed vertically in the cell, was substituted for the two electrodes, two rotations were observed which were uniformly dextro about the north-seeking pole of the rod, and lævo about the south-seeking pole. About the central neutral portion no rotations were observed. When the rod was covered with a thin coating of vaseline the rotations entirely disappeared as expected. Wartmann* observed similar rotations about soft-iron cylinders adhering to the poles of a magnet, and he ascribed them to electric currents in the liquid which proceed from the periphery of the cell radially to the surface of the rod.

The explanation of these rotations follows at once from what we know of the time-effects produced by the magnet. A higher potential is always produced at points of greater magnetization, causing electric currents in the liquid from the more strongly magnetized to the weaker parts of the iron.

Applying this fact to the exposed conical point electrode, we see that local electric currents exist from its vertex to the other parts of the surface, returning by way of the metal. In the case of the vertical rod, these currents pass from the poles

* Philosophical Magazine, xxx. p. 268 (1847).

at its ends, through the liquid, to the neutral portions, returning as before.

These currents*, under the influence of the poles themselves, would cause electromagnetic rotations of the liquid, as we find them. The mere mechanical influence of these rotations, as in the case when the liquid is artificially stirred, is to increase the chemical action upon the point, causing it to tend to act more like a zinc, which experiment confirms.

F. *Acids which attack Iron with the Evolution of Hydrogen.*

Professor Rowland had observed the "protective throw" with such acids to be extremely small, and difficult to detect except by very sensitive apparatus. The sensitive galvanometer was set up and every precaution taken against inductive effects. A telescope and scale were used in this part of the work.

Several substances were first examined, among them being hydrochloric acid, acetic acid, perchloric acid, chlorine water, copper sulphate, ferric chloride, sulphuric acid, &c., but as these observations added nothing to the results already obtained they are not given here.

After several trials a standard sulphuric-acid solution was made up as follows :—

Distilled water	10 grammes.
Gelatine	1 gramme.
C.P. Sulphuric acid, sp. gr. 1·826 ...	1·062 gramme.

More strongly acidulated gelatine would not harden, and weaker solutions gave too small effects.

The "protective throw" was detected, but the point very soon became completely covered with minute bubbles of hydrogen, so that the electrodes had to be cleaned constantly.

The effect of adding hydrogen dioxide to the solution was next tried, since this would facilitate the removal of the hydrogen as soon as formed†, which was thought to act merely mechanically.

When about 1 cubic centim. of H_2O_2 was added to the solution the "protective throw" became much more prominent, and the gas bubbles only appeared in small quantities after a considerable time. Further addition of small quantities

* The rotations produced in liquids by axial currents, *e. g.* currents coinciding with the direction of the magnetic lines of force as distinct from radial currents, have been studied by Dr. Gore (Proceedings of the Royal Society, xxxiii. p. 151).

† J. M. Weeren, *Berichte der Deutschen Chemischen Gesellschaft*, No. 11 (1891).

of the dioxide showed the "protective throw" to be very decided with sulphuric acid when the hydrogen is removed from the surface of the electrodes in this manner.

G. *The Electromotive Force.*

Several attempts were made to obtain the relation between the strength of field and the electromotive force developed in the "protective throw"; but it was difficult to obtain consistent readings owing to the trouble of balancing the original deflexion, and the small absolute values of this electromotive force when hardened gelatine was employed.

A curve was constructed, however, showing the variation of the galvanometer deflexion with the strength of field, using nitric-acid solution without gelatine. This is shown in fig. 2.

The readings were taken one after another as rapidly as possible, to eliminate the damping effects of the iron salts formed.

The curve exhibits the general character of the variation. In the region from about 3500 H to 8000 H the greatest rate of change occurred, and beyond 10,000 H the curve became nearly horizontal for the particular electrodes used. Curves were also constructed for the "concentration throw" on making the field under different conditions, and they were approximately right lines, more or less inclined according to the amount of iron salts present.

With the sulphuric-acid solution already given the electromotive force varied from 0·0033 to 0·0078 of a volt, while with the nitric-acid solution it became as great as 0·036 of a volt. In making all the solutions used with the different substances amounts were taken proportional to their particular molecular weights, and then halved or doubled until of suitable strength to give results with the galvanometer. It was thought possible at the beginning that this might lead to some relations between the protective results and the strengths of the particular solutions; but the general irregular character of the whole phenomenon prevented comparisons in this respect, and all that can be stated is, that both the "protective throw" and the concentration effect in general increased rapidly with the strength of the solution.

H. *Influence of a Periodic Magnetic Field upon the Cell.*

An experiment was made to determine the behaviour of the standard nitric-acid cell when the magnetic field was made and broken at regular intervals over a considerable time, and curves were drawn showing the variation of the "throw" with

time, and the fluctuation of the original deflexion caused by this treatment. The strength of field was about 11,000 H., and the experiment was conducted without compensating the original deflexion, and by making the field for one minute, then breaking for one minute, and so on.

One of the curves is shown in fig. 1 (III.), in which positive ordinates are values of the concentration throw at "make," and negative ordinates the values of the "protective throw."

Experimenting was not begun until the gelatine had completely hardened, and since the electrodes would tend to become polarized while the gelatine was hardening, the "protective throw" was very small, and soon masked by the concentration effects.

After about five minutes, making the field had very little effect at all, but began to show decided "concentration throws" ten minutes later, and these rapidly increased with time, as the curve indicates.

Considering the fluctuation of the original deflexion, the effect of this periodic field was to tend to reverse it, just as in the case of the uniform field in experiment B, but much more slowly, since the field was on but half the time in this case.

The cell also showed the iron salts almost entirely about the point, forming a thick black envelope.

I. *Summary.*

The principal results of this investigation may be summarized as follows:—

Whenever iron is exposed to chemical action in a magnetic field, there are two *directly opposite* influences exerted.

(*a*) The direct influence of the magnetized condition of the metal, causing the more strongly magnetized parts to be *protected* from chemical action.

This is exhibited in the phenomenon of the "protective throw," which is always in the direction to protect the more strongly magnetized parts of magnetic electrodes.

The "protective throw" is small, often requiring delicate apparatus to detect it, and is soon masked by the secondary concentration effects.

As to the absence of the "protective throw" with acids which attack iron with the evolution of hydrogen, the hydrogen acts merely mechanically, and when removed by adding to the solution small quantities of hydrogen dioxide, the "protective throw" becomes very decided.

In the curve, fig. 2, representing the variations of the "protective throw" with the strength of the magnetic field,

we trace at once the magnetization of the point-electrode. Since only the minute point was exposed to the liquid, it would become saturated for comparatively small magnetizing forces, and the curve indicates that this occurred at about 10,000 H., beyond which the curve becomes practically horizontal. This further establishes the direct connexion between this "throw" and the variation of the magnetization of the exposed point, and confirms the explanation of Professor Rowland, that it is due to the actual attraction of the magnet for the iron, and not to any molecular change produced by magnetization.

(*b*) The indirect influence of the magnet caused by the concentration of the products of the reaction about the more strongly magnetized parts of the iron.

This tends to produce a higher potential at the more strongly magnetized parts, and finally establishes permanent electric currents, which go in the liquid from the more strongly magnetized to the neutral parts of the iron.

This concentration-effect increases rapidly with the amount of iron salts present and the fluidity of the solution.

The convection-currents in the liquid are themselves a consequence of this same concentration, being electromagnetic rotations produced by the action of the magnet upon the local electric currents between different parts of the iron.

As to the permanent current due to the magnet which is finally set up between the electrodes, as shown in fig. 1 (II.), it is probably owing to a change in the character of the reaction produced by the concentration of the iron salts about the more strongly magnetized parts, which would tend to cause a ferrous instead of a ferric reaction to take place, and thus increase the electromotive force.

Physical Laboratory, Johns Hopkins University,
May 1892.

Note.—Since the completion of the above investigation, a number of experiments have been performed similar to those of Professor Remsen. Starting with the known existence and direction of the electric currents in the liquid, it was thought that these might lead to some explanation of the peculiar form of deposit in equipotential lines. A number of interesting facts have been noted, but they are withheld for further experiments. G. O. S.

XLIX. *On the Applicability of* Lagrange's *Equations of Motion in a General Class of Problems; with especial reference to the Motion of a Perforated Solid in a Liquid.* *By* CHARLES V. BURTON, *D.Sc.**

1. LET $\psi, \phi, \ldots$ be *some only* of the coordinates of a material system, so that when the values of $\psi, \phi, \ldots$ are given the whole configuration is *not* completely determinate. But suppose it known that the kinetic energy T can be expressed *as a homogeneous quadratic function of* $\dot{\psi}, \dot{\phi}, \ldots$ *only*; so that we may write

$$\left.\begin{array}{l} 2\mathrm{T} = (\psi\psi)\dot{\psi}^2 + 2(\psi\phi)\dot{\psi}\dot{\phi} + \ldots \\ (\psi\psi),\ (\psi\phi), \ldots \text{ are functions of } \psi, \phi, \ldots \text{ only} \end{array}\right\} \quad . \quad . \quad (1)$$

We also suppose it known *that* (1) *continues to hold good so long as the only* (*generalized*) *forces and impulses acting are of types corresponding to*

$$\psi, \phi, \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

2. Suppose, now, that such impulses of these types were to act on the system that $\dot{\psi}, \dot{\phi}, \ldots$ were all reduced to zero; the expression for the kinetic energy would accordingly vanish, and the system would be at rest. By supposing the last operation to be reversed, we see that *the motion at any instant could be produced from rest by impulses of the types corresponding to*

$$\psi, \phi, \ldots \textit{ only}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

3. Let x, y, z be the Cartesian coordinates at time τ of a mass-element m referred to fixed axes, and let T be the kinetic energy of the system at the same instant. Further, let A be the "action" when the system moves without additional constraint from one configuration to another, and $\mathrm{A} + \delta\mathrm{A}$ the action when by workless constraints the path is slightly modified, so that in place of the coordinates x, y, z we have $x + \delta x, y + \delta y, z + \delta z$. Then †

$$\begin{aligned} \delta\mathrm{A} = \{\Sigma m(\dot{x}\delta x + \dot{y}\delta y + \dot{z}\delta z)\} - [\Sigma m(\dot{x}\delta x + \dot{y}\delta y + \dot{z}\delta z)] \\ + \text{ a term which necessarily vanishes}; \quad . \quad . \quad (4) \end{aligned}$$

where [ ] and { } denote the values of the quantities enclosed at the beginning and end of the motion considered.

Suppose further that, both at the beginning and at the end, the values of $\psi, \phi, \ldots$ are the same for the one motion as for

* Communicated by the Physical Society: read March 10, 1893.

† Thomson and Tait's 'Natural Philosophy,' 2nd edit. Part I. § 327.

the other, so that initially and finally $\delta\psi, \delta\phi, \ldots$ are all zero. *It does not follow that all the* δx, δy, δz*'s are zero*; but

$$\Sigma m(\dot{x}\delta x + \dot{y}\delta y + \dot{z}\delta z)$$

is the so-called "virtual moment" of the actual momenta in the hypothetical displacement δx, δy, δz; that is, the virtual moment, in the same displacement, of the impulse necessary to produce the actual motion from rest. In virtue of (3), therefore, and of the initial and final vanishing of $\delta\psi, \delta\phi, \ldots$ we see that the bracketed terms of (4) must both be zero; hence

The increment δA *vanishes and* A *has a stationary value for all worklessly effected variations of path which leave the initial and final values of* $\psi, \phi, \ldots$ *unaltered.* . (5)

4. Lagrange's equations for the coordinates $\psi, \phi, \ldots$ may now be written down at once, since the investigation of Thomson and Tait* becomes applicable to the present case without modification. It will be noticed that in their equations $(10)^{\text{v}}$ and $(10)^{\text{vi}}$, § 327, the sign of $\partial V/\partial\psi$ should be reversed.

We have thus a perfectly general proof of the proposition: *If the kinetic energy of a material system can be expressed as a homogeneous quadratic function of certain generalized velocities* $\dot{\psi}, \dot{\phi}, \ldots$ *only, the coefficients being functions of* $\psi, \phi, \ldots$ *only, and if this remains always true so long as the only forces and impulses acting are of types corresponding to* $\psi, \phi, \ldots$, *the equations of motion for the coordinates* $\psi, \phi, \ldots$ *may be written down from this expression for the energy, in accordance with the Lagrangian rule. Provided only that the stated conditions are satisfied, we need not consider whether the whole configuration is determined by the values of* $\psi, \phi, \ldots$, *or what is the nature of the ignored coordinates.* . . . . . (A)

5. Passing over the known application of this result to the motion of solids through an irrotationally and acyclically moving liquid, we come to the more general case of a perforated solid, with liquid irrotationally circulating through the apertures. Take as coordinates any six $\theta, \theta', \ldots$ which determine the position of the solid, together with $\chi, \chi', \ldots$ equal in number (m) to the apertures; each χ being the volume of liquid which, starting from a given configuration, has flowed across some one of the m geometrical surfaces, required to close the apertures, these surfaces being supposed to move along with the solid.

Of course the coordinates $\theta, \theta', \ldots \chi, \chi', \ldots$ are insufficient

* *Loc. cit.*

to determine the entire configuration of the system (including the positions of all the particles of liquid); but we shall see immediately how, in virtue of the proposition (A), Lagrange's equations may be written down.

6. Since an increment $\delta\chi$ in one of the coordinates χ is the volume of liquid which flows across a barrier-surface (*i. e.*, which flows through an aperture *relatively to the solid*), the generalized force corresponding to χ must be conceived of as a uniform pressure exerted over the said geometrical surface, by means of some immaterial mechanism attached to the solid; while the impulse corresponding to χ is of course a uniform impulsive pressure applied in the same manner. From hydrodynamical considerations we know that the measure of such an impulsive pressure is $\rho\delta\kappa$, where ρ is the density of the fluid, and $\delta\kappa$ the change produced in the circulation through the corresponding aperture.

Hence the impulses corresponding to $\chi, \chi', \ldots$ are

$$\kappa\rho,\ \kappa'\rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\kappa, \kappa', \ldots$ are the circulations through the various apertures.

7. Now when the motion of the liquid is irrotational, we have

T = a homogeneous quadratic function of $\dot{\theta}, \dot{\theta}', \ldots \kappa, \kappa' \ldots$ only; coefficients functions of $\theta, \theta' \ldots$ only;

$\dot{\chi}, \dot{\chi}', \ldots$ = homogeneous linear functions of $\theta, \theta', \ldots$ $\kappa, \kappa', \ldots$ only; coefficients functions of $\theta, \theta', \ldots$ only.

Since the $\dot{\chi}$'s are equal in number to the κ's, let us suppose the last-written system of linear equations to be solved for the κ's in terms of the $\dot{\chi}$'s; we then have

$\kappa, \kappa', \ldots$ = homogeneous linear functions of $\dot{\theta}, \dot{\theta}', \ldots \dot{\chi}, \dot{\chi}', \ldots$ only; coefficients functions of $\theta, \theta', \ldots$ only.

Substituting in the expression for T we get

T = a homogeneous quadratic function of $\dot{\theta}, \dot{\theta}', \ldots \dot{\chi}, \dot{\chi}', \ldots$ only; coefficients functions of $\theta, \theta', \ldots$ only.

This, then, remains true so long as the motion of the liquid is irrotational; in other words, so long as the only forces and impulses acting are of types corresponding to $\theta, \theta', \ldots$ (since these are applied to the solid), $\chi, \chi', \ldots$ (since these are uniform over the barriers, by § 6).

If we identify $\psi, \phi, \ldots$ with the coordinates $\theta, \theta', \ldots \chi, \chi', \ldots$ of the present example, we see that the proposition (A) of § 4 is immediately applicable to this case. We may therefore

ignore all other coordinates, and from the kinetic energy expressed as a function of $\dot{\theta}, \dot{\theta}', \ldots \dot{\chi}, \dot{\chi}', \ldots$ write down the Lagrangian equations for $\theta, \theta', \ldots$ and, if we wish, for $\chi, \chi', \ldots$ also. These latter, however, are less directly intelligible, since in general they involve finite pressures continuously acting over geometrical surfaces drawn through the liquid.

8. If we wish to picture the application of the principle of least action (§ 3) to the present case, we may proceed as follows:—Let the system start from the configuration (I.) and move without additional constraint or influence to the configuration (II.). Then let it start again from the configuration (I.) with the same velocities as before, and during the motion let infinitesimal additional forces act on the solid, while infinitesimal pressures, uniform over each barrier-surface, are impressed on the liquid; the total rate at which the additional influences do work being at each instant zero. Further, let the additional influences be so adjusted that the system, after following a slightly different path, passes through a configuration such that $\theta, \theta', \ldots \chi, \chi', \ldots$ are all the same as for (II.). Then, to pass from the configuration (II.) to the present configuration requires no displacement of the solid, and only such displacement of the liquid that the *total* volume which crosses any barrier-surface is zero. In such a change of configuration impulses of the types $\theta, \theta', \ldots \chi, \chi', \ldots$ would have no "virtual moment," just as forces applied to the solid and uniform pressures applied to the barrier-surfaces would give rise to no virtual work.

9. At this stage it will be convenient to replace $\dot{\theta}, \dot{\theta}', \ldots$ by the components u, v, w of linear velocity and p, q, r of angular velocity, which determine the instantaneous motion of the solid along and about axes fixed in itself. The Lagrangian equations for the six coordinates $\theta, \theta', \ldots$ must accordingly be replaced by the forms suitable to moving axes. The expression for the energy in terms of the velocities now becomes a homogeneous quadratic function of $u, v, w, p, q, r, \dot{\chi}, \dot{\chi}', \ldots$ in which all the coefficients are known to be constants.

Let us apply the method due to Routh *, and *modify* this function with respect to the coordinates $\chi, \chi', \ldots$ If T be the value of the kinetic energy in terms of the velocities alone, the modified function (*i. e.* the kinetic part of Routh's modified Lagrangian function)

$$T' = T - \frac{\partial T}{\partial \dot{\chi}}\dot{\chi} - \frac{\partial T}{\partial \dot{\chi}'}\dot{\chi}' - \ldots = T - \kappa\rho\chi - \kappa'\rho\dot{\chi}' - \quad . \; . \; (7)$$

* 'Rigid Dynamics,' vol. i. chap. viii.

from (6). It is further known that the whole energy of the system

$$=\mathrm{E}+\mathrm{K}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where E is a function of $u \ldots, p \ldots,$ only, and K is a function of the momenta $\kappa\rho$ only. Suppose, now, that the solid were brought to rest by forces applied to it alone: E would vanish along with u, v, w, p, q, r, while the circulations κ, and consequently also K, would remain unaltered. The generalized velocities $\dot{\chi}, \dot{\chi}', \ldots$ would in general have changed, becoming, let us suppose $\dot{\chi}_0, \dot{\chi}_0', \ldots$ and the kinetic energy would accordingly have become

$$\mathrm{K}=\tfrac{1}{2}(\kappa\rho\dot{\chi}_0+\kappa'\rho\dot{\chi}_0'+\ldots). \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now let

$$\dot{\chi}=\dot{\chi}_0+\dot{\chi}_1, \quad \dot{\chi}'=\dot{\chi}_0'+\dot{\chi}_1', \quad . \quad . \quad . \quad . \quad . \quad (10)$$

so that each $\dot{\chi}_1$ is that part of the flux of liquid (volume per unit time) which takes place across a barrier-surface owing to the motion of the solid itself.

Having regard to (8), (9), and (10) our equation (7) for T′ becomes

$$\mathrm{T}'=(\mathrm{E}+\mathrm{K})-2\mathrm{K}-\kappa\rho\dot{\chi}_1-\kappa'\rho\dot{\chi}_1'. \quad . \quad . \quad . \quad (11)$$

Let us write for the velocity-potential of the *acyclic* motion

$$\Phi=u\phi_u+v\phi_v+w\phi_w+p\phi_p+q\phi_q+r\phi_r, \quad . \quad . \quad (12)$$

and for the value of $\dot{\chi}_1$ across the barrier-surface σ we have

$$\dot{\chi}_1=\iint\left\{\frac{\partial\Phi}{\partial\nu}-[ul+vm+wn+p(ny-mz)\right.$$
$$\left.+q(lz-nx)+r(mx-ly)]\right\}d\sigma, \quad . \quad . \quad . \quad (13)$$

where x, y, z are the coordinates of the element $d\sigma$ and l, m, n are the direction-cosines of its normal ν, all referred to the system of axes fixed in the solid. From (12) and (13) substitute in (11); thus

$$\mathrm{T}'=\mathrm{E}-\mathrm{K}+u\Sigma\kappa\rho\iint\left(l-\frac{\partial\phi_u}{\partial\nu}\right)d\sigma+\text{similar terms in } v, w,$$
$$+p\Sigma\kappa\rho\iint\left(ny-mz-\frac{\partial\phi_p}{\partial\nu}\right)d\sigma+\text{similar terms in } q, r, \quad . \quad (14)$$

where the summation refers to the m barriers.

Remembering (8) it will be seen that T′ is now expressed in the proper form, namely as a function of u, v, w, p, q, r, and

the momenta $\kappa\rho$, $\kappa'\rho, \ldots$ only. By means of the relations

$$\frac{d}{dt}\frac{\partial T'}{\partial u} - r\frac{\partial T'}{\partial v} + q\frac{\partial T'}{\partial w} = X, \text{ \&c., \&c.}$$

$$\frac{d}{dt}\frac{\partial T'}{\partial p} - w\frac{\partial T'}{\partial v} + v\frac{\partial T'}{\partial w} - r\frac{\partial T'}{\partial q} + q\frac{\partial T'}{\partial r} = L, \text{ \&c., \&c.}$$

the equations of motion of the solid can at once be written down. $X, \ldots, L, \ldots$, are of course impressed force- and couple-constituents.

10. Since the kinetic energy due to any number of perforated solids, moving in circulating liquid, can be divided into two parts, of which one is a function of the component velocities of the solids alone, and the other a function of the circulation-momenta alone, the above method may obviously be extended; in fact a slight change in (14) will render it at once applicable to the more general case. We shall have, evidently,

$$T' = E - K + \Sigma u \Sigma \kappa\rho \iint \left(l - \frac{\partial \phi_u}{\partial \nu}\right) d\sigma + \text{similar terms in } v, w,$$

$$+ \Sigma p \Sigma \kappa\rho \iint \left(ny - mz - \frac{\partial \phi_p}{\partial \nu}\right) d\sigma + \text{similar terms in } q, r, \quad (15)$$

where E is still the energy due to the motion of the solids and the acyclic motion of the liquid, and K the energy due to the circulations. In each barrier-term the first Σ denotes summation with respect to all the solids, and for each u or p, &c., the second Σ denotes summation with respect to all the barriers of the system.

These hydrodynamical results are not new, but the method of proof is in some respects different from anything that has yet been given, and will, I hope, be found intelligible and fairly simple. In an admirable memoir, just communicated to the Physical Society, Mr. Bryan has given a direct hydrodynamical proof of the equations holding good for the motion of the system in question; but it seemed to me also desirable that the problem should be rigorously treated by the method of generalized coordinates, avoiding any assumption as to the impulse of the cyclic motion, and proceeding entirely from the principles established by Lagrange, and extended by Hamilton, Routh, and Hayward.

When this paper was in proof it contained some remarks on the ignoration of coordinates, as treated in Thomson and Tait's 'Natural Philosophy'*. Calling $\chi, \chi', \ldots$ the inde-

* Part I. § 319, example G.

pendent coordinates which, together with ψ, ϕ, ... determine the whole configuration of the system in §§ 1, ..., it was suggested that, in hydrodynamical and kindred applications, there was a difficulty in proving that $\partial T/\partial\chi$, $\partial T/\partial\chi'$, ... were all zero.

But the difficulty, if indeed it should exist, is easily removed. For since the actual motion at any instant could be generated from rest by impulses of types corresponding to ψ, ϕ, ... only, we have throughout the motion

$$\partial T/\partial\dot{\chi}=0, \quad \partial T/\partial\dot{\chi}'=0, \ldots;$$

and by the Lagrangian equations for χ, χ', ..., since all the generalized forces are of types corresponding to ψ, ϕ, ..., we get

$$\frac{d}{dt}\frac{\partial T}{\partial\dot{\chi}}-\frac{\partial T}{\partial\chi}=0, \quad \frac{d}{dt}\frac{\partial T}{\partial\dot{\chi}'}-\frac{\partial T}{\partial\chi'}=0, \ldots$$

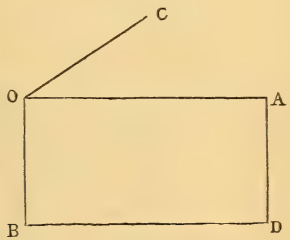
whence

$$\frac{\partial T}{\partial\chi}=0, \quad \frac{\partial T}{\partial\chi'}=0, \ldots.$$

L. *Note on the Finite Bending of Thin Shells.* *By* A. B. Basset, *M.A., F.R.S.**

1. When a thin shell of any form is bent in any manner, the most convenient way of obtaining the equations of equilibrium is to consider the stresses which act on a small element of the shell bounded by four lines of curvature on the *deformed* middle surface. If O A D B be a small curvilinear

Fig. 1.



rectangle bounded by the four lines of curvature O A, A D, D B, and B O, the stresses across the section A D (as pointed out in my previous papers †) consist of the following

* Communicated by the Author.

† Proc. Lond. Math. Soc. vol. xxi. pp. 33 and 53; Phil. Trans. 1890, p. 433.

quantities, viz.:—

T_1 = a tension across A D parallel to O A;
M_2 = a tangential shearing-stress along A D;
N_2 = a normal shearing-stress parallel to OC;
G_2 = a flexural couple from C to A, whose axis is parallel to A D;
H_1 = a torsional couple from B to C, whose axis is parallel to O A.

Similarly the stresses which act across the section B D consist of:—

T_2 = a tension across B D parallel to O B;
M_1 = a tangential shearing-stress along B D;
N_1 = a normal shearing-stress parallel to O C;
G_1 = a flexural couple from B to C, whose axis is parallel to B D;
H_2 = a torsional couple from C to A, whose axis is parallel to O B.

By resolving the stresses and bodily forces (such as gravity and the like), which act upon the element, parallel to the axes O A, O B, and O C, and by taking moments about these lines, we obtain the six equations of equilibrium of the element; but as these six equations connect ten unknown quantities, namely the ten stresses which act across the sides of the element, they are insufficient for the solution of the problem.

2. In the case of a bell, or of a railway bridge which is thrown into a state of oscillation by a passing train, the displacements are all small quantities, and under these circumstances the ten sectional stresses can be expressed in terms of the displacements of a point on the middle surface and their differential coefficients; and owing to the fact that these displacements are *small*, we may neglect their squares and products when determining the stresses, and their cubes &c. when determining the potential energy due to strain. There is, however, another class of problems of considerable importance in which the deformation is finite instead of infinitesimal; and to such problems the theory of thin shells is inapplicable.

3. An ordinary clock-spring is one of the most familiar examples of the finite bending of a thin plate or shell. Such springs consist of a naturally curved steel strip whose thickness is somewhere about one thirtieth of an inch, and whose breadth is from an eighth to a quarter of an inch according to the size of the clock; and when the clock is wound up an amount of bending takes place which it would be unsafe to treat as infinitesimal. The hair-spring of a watch also

involves a case of finite bending; but as its cross section is approximately square, the theory of the bending of wires* would be more applicable. Similar examples, such as spring balances and other mechanical appliances where springs are employed, will readily suggest themselves; and the question whether the theory of wires or the theory of thin shells is most appropriate depends upon the nature of the spring. If the cross section does not differ much from a circle or a square, the former theory would appear to be the most applicable; if, on the other hand, the breadth of the spring is considerable compared with its thickness, it would be better to regard it as a thin shell.

When the natural form of a spring is a plane curve, and the spring is bent into another plane curve, the problem may be completely solved by the methods explained in chapter viii. of my 'Elementary Treatise on Hydrodynamics and Sound.' The mathematical treatment is the same whether the spring be regarded as a wire or as a thin strip of metal like a clock-spring; the only difference being that the flexural rigidity is different in the two cases. If, however, a piece of clock-spring is twisted as well as bent, or a thin plate or shell is deformed in a finite manner, the solution of the problem presents difficulties of a rather formidable character.

4. Whenever the deformation is finite, the displacements of a point on the middle surface are *not* small quantities whose squares and higher powers may be neglected, and therefore it is useless to attempt to express the stresses in terms of these quantities; but since any deformation involves a change in the values of certain geometrical quantities, such as the curvature and torsion of certain lines drawn on the middle surface, the most appropriate course to pursue would be to endeavour to express the stresses in terms of such geometrical quantities.

There is one class of problems which can often be solved without much difficulty, which occurs when a plane surface is bent without extension into a developable surface; or when a developable surface is bent into a plane, or into some other developable surface such that the lines of curvature on the old surface are lines of curvature on the deformed surface. This method can generally be applied when a plane plate is bent into a conical or cylindrical surface; but it could not be applied in the case of a right circular cone which is bent into a cone whose lines of curvature are not identical with those of the former cone.

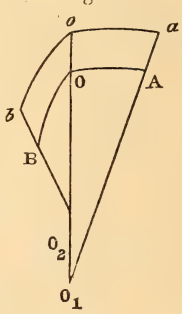
The success of this method, in cases where it can be applied, depends upon the circumstance that the flexural couples G_1,

* See Proc. Lond. Math. Soc. vol. xxiii. p. 105.

G_2 can be expressed in terms of the changes of curvature, and also that in the special cases alluded to a sufficient number of the ten stresses are zero to enable the remainder to be determined by means of the general equations of equilibrium.

5. We shall now determine these couples, using Thomson and Tait's notation for stresses and elastic constants, and Love's notation for strains.

Fig. 2.



Let O A, O B be two lines of curvature on the middle surface of the *undeformed* shell; O_1, O_2 the centres of principal curvature; let oa, ob be the curves in which the planes OAO_1, OBO_2 meet any layer of the shell. Let ρ_1, ρ_2 be the principal radii of curvature at O, let $Oo=\eta$, and let $2h$ be the thickness of the shell. Also let accented letters denote the strained positions of the various points.

If P denote the traction along oa, and R the normal traction along Oo,

$$\begin{aligned} P &= (m+n)\sigma_1 + (m-n)(\sigma_2+\sigma_3) \\ &= 2n\{(1+E)\sigma_1 + E\sigma_2\} + ER, \quad . \quad . \quad . \quad . \quad (1) \end{aligned}$$

where

$$E=(m-n)/(m+n).$$

Now

$$\sigma_1 = \frac{o'a'-oa}{oa},$$

and

$$\frac{oa}{OA} = 1+\frac{\eta}{\rho_1}, \quad \frac{o'a'}{O'A'} = 1+\frac{\eta'}{\rho_1'}, \quad \eta' = \eta(1+\sigma_3).$$

Since we neglect the extension of the middle surface, $O'A'=OA$, whence

$$\begin{aligned} \sigma_1 &= \frac{\eta'/\rho_1' - \eta/\rho_1}{1+\eta/\rho_1} = \eta\left(\frac{1}{\rho_1'}-\frac{1}{\rho_1}\right) + \frac{\eta\sigma_3}{\rho_1'} \\ &= \eta\left(\frac{1}{\rho_1'}-\frac{1}{\rho_1}\right) + \frac{\eta}{\rho_1'}\left\{\frac{R}{m+n} - E(\sigma_1+\sigma_2)\right\} \quad . \quad . \quad (2) \end{aligned}$$

Similarly,

$$\sigma_2 = \eta\left(\frac{1}{\rho_2'}-\frac{1}{\rho_2}\right) + \frac{\eta}{\rho_2'}\left\{\frac{R}{m+n} - E(\sigma_1+\sigma_2)\right\}. \quad . \quad (3)$$

The value of G_2 is

$$G_2 = \int_{-h}^{h} P\eta\, d\eta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now, according to the fundamental hypothesis of my former papers it follows that, *provided there is no external pressure*, R must be a quadratic function of h and η, and consequently the retention of R will lead on integration to terms in G_2 of a higher order than h^3, which are to be neglected, since the solution we require is an approximate one which does not contain higher powers of h than the cube. Accordingly if we substitute the values of σ_1, σ_2 from (2) and (3) in (1), and the resulting value of P in (4) and integrate, we shall obtain

$$G_2 = \frac{4}{3} nh^3 \left\{ (1+E)\left(\frac{1}{\rho_1'} - \frac{1}{\rho_1}\right) + E\left(\frac{1}{\rho_2'} - \frac{1}{\rho_2}\right) \right\}. \quad . \quad (5)$$

Similarly,

$$G_1 = -\int_{-h}^{h} Q\eta \, d\eta,$$

which gives

$$G_1 = -\frac{4}{3} nh^3 \left\{ (1+E)\left(\frac{1}{\rho_2'} - \frac{1}{\rho_2}\right) + E\left(\frac{1}{\rho_1'} - \frac{1}{\rho_1}\right) \right\}. \quad . \quad (6)$$

Equations which are equivalent to (5) and (6) have been given by more than one writer on elasticity; but attention has not always been called to the fact that they depend upon the express conditions that the surfaces of the shell are free normal pressures, and also that the extension of the middle surface may be neglected.

When a plane plate is bent into a developable surface $\rho_1 = \rho_2 = \infty$; also one of the quantities ρ_1', or ρ_2' (say ρ_2') is infinite; whence (5) and (6) become

$$\left.\begin{aligned} G_2 &= \tfrac{4}{3} nh^3 (1+E)/\rho_1' \\ G_1 &= -\tfrac{4}{3} nh^3 E/\rho_1' \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where G_2 is the couple about a generating line of the developable.

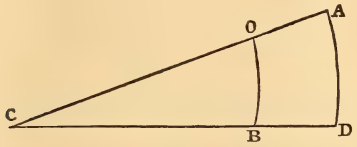
Since the extension of the middle surface is neglected, equations (5) and (6) would not apply to the case of a plane plate deformed into a surface such as a portion of a sphere.

7. As an example of the preceding method, we shall consider the case of a plane plate of thickness $2h$, which is bounded by two radii CA, CD, and two arcs OB, AD of concentric circles; and we shall inquire whether it is possible to bend this plate into a portion of a right circular cone in which OA, BD are generators, and OB, AD are circular sections.

We shall assume for trial that the bending may be effected by means of tensions, normal shearing stresses, and flexural

couples applied to the edges; so that the tangential shearing stresses and the torsional couples are zero.

Fig. 3.



Let α be the semi-vertical angle of the cone, r the distance of any point on OADB from C. Then

$$\rho_1'=\rho_1'=\infty\ ;\ \rho_2=0\ ;\ \rho_2'=r\tan\alpha\ ;$$

whence

$$G_2=\tfrac{4}{3}nh^3Er^{-1}\cot\alpha,$$

$$G_1=-\tfrac{4}{3}nh^3(1+E)r^{-1}\cot\alpha.$$

The equations of equilibrium are

$$\left.\begin{aligned}
&\frac{d}{dr}(T_1r)-T_2=0,\\
&\frac{dT_2}{d\phi}+N_1\cos\alpha=0,\\
&\frac{d}{dr}(N_2r)\sin\alpha+\frac{dN_1}{d\phi}-T_2\cos\alpha=0,\\
&\frac{dG_1}{d\phi}+N_1r\sin\alpha=0,\\
&\frac{d}{dr}(G_2r)-N_2r+G_1=0.
\end{aligned}\right\}\quad . \quad . \quad . \qquad (8)$$

Let

$$\tfrac{4}{3}nh^3(1+E)\cot\alpha=k,$$

then

$$G_1=-k/r,$$

whence

$$N_2=-k/r^2,\ N_1=0,$$

whence

$$T_2=k\tan\alpha/r^2,$$

and therefore

$$T_1=\frac{A}{r}-\frac{k\tan\alpha}{r^2},$$

where A is the constant of integration.

From these equations we see that all the stresses are per-

fectly determinate except T_1. If $CO=a$, $CA=b$, and T_a, T_b denote the tensions along OB, AD, we have

$$\left.\begin{aligned} T_a &= \frac{A}{a} - \frac{k \tan \alpha}{a^2} \\ T_b &= \frac{A}{b} - \frac{k \tan \alpha}{b^2} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

from which it appears that either T_a or T_b may, if we please, be made zero, provided the other be properly determined.

The above results would also apply to a belt of a complete cone, bounded by two circular sections.

LI. *Bolometric Investigations on the Intensity of Radiation by Rarefied Gases under the Influence of Electric Discharge. By* Knut Ångström*.

ONE of the peculiar difficulties attending the quantitative determination of the amount of energy radiated by gases in vacuum-tubes is the extreme feebleness of its intensity. In his recent work in this field, executed at the Hochschule at Stockholm, Prof. Ångström attacked the problem by the bolometric method, which, although leaving something to be desired as regards sensitiveness, led to some important results. Another obstacle lay in the well-known difficulty of obtaining the gases in a state of such purity that the spectrum exhibited by the discharge through them in a vacuum-tube showed no foreign admixture, such as the carbon-bands seen whenever grease is used for joining surfaces, or where the flame touches in the process of soldering.

The discharge-tube used for the most careful experiments was thoroughly cleaned after soldering-in two electrometer-terminals, and attaching two short lengths of tubing at right angles near each end. The latter were to receive the electrodes, whose construction required particular care. Into a short capillary tube a piece of platinum wire was introduced from one end and a piece of thoroughly cleaned aluminium wire from the other. The tube was then heated so as to form an air-tight junction between the two wires, and was then fitted into a glass plate. After removing all grease the tube covering the aluminium wire was cut off, so that the latter acted as a perfectly clean electrode, and the glass plate holding it was fitted on to the short tube attached to the discharge-

* Abstract from Wiedemann's *Annalen*, No. 3, 1893, by E. E. Fournier d'Albe, B.Sc., Royal College of Science.

tube. The joints were made air-tight by means of sodium silicate, which proved to be a highly useful cement, and did not give rise to any impurities. Short lengths of tubing containing mercury were placed round the platinum wires to convey the current to the electrodes.

The behaviour of four gases only was investigated, viz. hydrogen, oxygen, nitrogen, and carbonic oxide. Hydrogen and oxygen were prepared by electrolysis of pure newly-distilled water acidulated with phosphoric acid. The nitrogen was obtained by passing pure air over heated copper-turnings reduced by hydrogen. Carbonic oxide was prepared by the reaction of sulphuric and oxalic acids, and purified by passing through caustic potash. In producing these gases all rubber tubes were dispensed with, and the different parts of the generating apparatus were soldered together.

The discharge-tube was connected through a Kundt glass spring and a set of cleaning-tubes to the tube used for introducing the gas, a mercury-valve, and the air-pump. The mercury-valve consisted of a U-tube communicating at the bottom with a long tube full of mercury. By varying the level of the mercury by means of a reservoir the valve could be opened and closed. The tube for introducing the gases corresponded in the main to Cornu's arrangement. A vertical glass tube is filled with mercury whose level can be varied by means of a reservoir connected through a flexible tube, as in the case of the mercury-valve. At a point some distance from the bottom is attached a capillary U-tube, the end of which, in the process of filling, is introduced into a small reservoir containing the gas. Lowering the mercury establishes a connexion with the discharge-tube through the drying-tubes, and on raising the level the gas is shut off from the atmosphere.

The current was furnished by a battery of 800 small Planté accumulators, regulated by means of a liquid resistance consisting of cadmium iodide dissolved in amyl alcohol, and measured by a dead-beat reflecting-galvanometer. The fall of potential in the discharge-tube was measured by a Mascart quadrant-electrometer.

The bolometer used for the experiments consisted of two gratings cut out of tinfoil mounted in ebonite frames. These frames were placed one behind the other in a tube with double walls, the posterior one being protected from radiation by a small double screen. Four diaphragms were mounted in the tube in front of the gratings, to diminish air-currents. The grating absorbing the radiation occupied a circular space of 16 millim. diameter. It was blackened by precipitated

platinum and smoke. The four branches of the Wheatstone-bridge arrangement, of which the gratings formed two, had each a resistance of about 5 ohms. In order to be able to rapidly test the sensitiveness of the combination, a constant resistance was introduced as a secondary circuit into one of the branches. The opening or closing of this circuit usually made a difference of 75 scale-divisions. If not, the reading was reduced to that standard sensitiveness.

The bolometer was separated from the end of the discharge-tube by a double screen with a perforation, inside which was suspended a small screen. This was quickly pulled up to expose the bolometer. The strength of current through the discharge-tube was measured by the galvanometer, the difference of potential within it by the electrometer, and the deflexion of the galvanometer in the bolometer circuit was read from minute to minute. The latter gradually increased, owing to the warming of the walls of the discharge-tube. By suddenly breaking the current and again observing the bolometer the radiation of the tube-walls was eliminated. Another method of elimination was by interposing a plate of alum about 4 millim. thick, which totally absorbed the radiation from the glass. Another source of error was the reflexion from the walls of the tube. The end of the tube opposite the bolometer was closed by a plane-parallel plate of rock-salt. This occasioned a loss by reflexion, whereas the other surfaces entailed a gain. Both were corrected by introducing a small copper box heated by steam circulation into a tube of the same construction as the discharge-tube, observing the bolometer deflexions, and repeating with the box alone.

Prof. Ångström states his main results as follows:—

1. For a given gas and a given pressure the radiation of the positive light is proportional to the intensity of the electric current.

2. For a given gas and pressure the composition of the radiation is constant and independent of the strength of current.

3. On increasing the pressure of the gas, the total radiation for a given strength of current increases as a rule, slowly at low, more rapidly at high pressures. At the same time the composition of the radiation changes, inasmuch as the ratio of the intensity of the shorter waves to the total radiation decreases. Thus the distribution of the intensity in the spectrum changes in such a manner that with diminishing pressure the intensity of radiation increases for the shorter wave-lengths.

4. The ratio between the intensity of total radiation and

the current-work increases continuously with diminishing pressure of gas.

5. The useful optical effect of the radiation (here given by the ratio of the intensities of the radiation passing through the alum plate and the total radiation respectively) is very high for some of the gases at low pressure (about 90 per cent. for nitrogen). But the useful optical effect of the work spent is not very great (about 8 per cent. for nitrogen of 0·1 millim. pressure).

6. The intensity of total radiation must be considered as a secondary effect of the discharge, and depends upon the molecular constitution of the gas.

7. Whatever views we hold concerning the nature of the gaseous discharge, this investigation appears to confirm the hypothesis of Hittorf, E. Wiedemann, and others, that the radiation is not a pure function of the temperature of the gases, but must be regarded as anomalous ("irregular," "luminescence").

If we call "irregular" a radiation in which the spectroscopic distribution of the energy is anomalous, there are certain facts observed by Prof. Ångström which lead to the conclusion that the radiation in question is irregular. The radiation did not show any relation to the absorptive power of the gas at ordinary temperatures. Again, the radiation,—which in nitrogen at 2 millim. pressure is still rich in dark rays,—rapidly changes in quality when the pressure decreases, and at 1 millim. consists almost exclusively of light radiation. Prof. Ångström supposes that the radiation of the gas during electric discharge consists of two parts, one of them regular, the other irregular. With decreasing pressure the former decreases, whilst the irregular radiation increases in proportion as the motions are less obstructed by the mass of the gas. At constant pressure a certain portion of the energy in each molecule is converted into radiation; as the strength of the current increases, the number of active molecules, and hence also the radiation, increases in the same proportion as the current. The number of active molecules being relatively small, the damping effect of the rest may be taken as constant, and the composition of the radiation remains practically unaltered as the current increases. On increasing the pressure, however, the damping effect changes, the anomalous dispersion is more easily transformed into a normal one, and the radiation becomes richer in infra-red rays. A greater proportion of the energy supplied is spent in heating, and for the same current-work the total radiation decreases with increasing pressure.

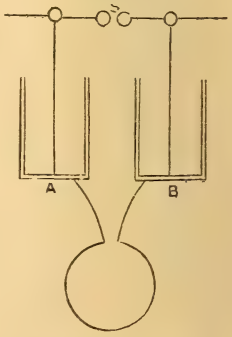
But in view of the difficulties of the investigation, the paucity of available material, and the approximate nature of the results in this almost unexplored field, no final decision can as yet be arrived at. A tabulation and a graphic representation of the results, with diagrams of the apparatus and a full discussion of methods and corrections, will be found in the original paper.

LII. *Luminous Discharges in Electrodeless Vacuum-Tubes.* *By* E. C. Rimington*.

SINCE reading a paper in conjunction with Mr. E. W. Smith on November 25th, 1892, before this Society†, on "Experiments in Electric and Magnetic Fields, Constant and Varying," the Author's attention has been drawn to a paper contributed by Mr. Tesla to the 'Electrical Engineer' of New York, July 1st, 1891, in which the luminous ring-shaped discharge obtained when a Leyden jar is discharged through a coil of wire surrounding an exhausted bulb is attributed to the electrostatic action of the surrounding wire, and not to the electric stress set up in the rarefied dielectric in consequence of the rapidly oscillating magnetic induction through the bulb.

As one experimental proof of this assertion Mr. Tesla gives the following experiment :—"An ordinary lamp-bulb was surrounded by one or two turns of thick copper wire, and a luminous circle excited by discharging the jar through this primary. The lamp-bulb was provided with a tinfoil coating on the side opposite to the primary, and each time the tinfoil coating was connected to the ground, or to a large object, the luminosity of the circle was considerably increased."

Fig. 1.

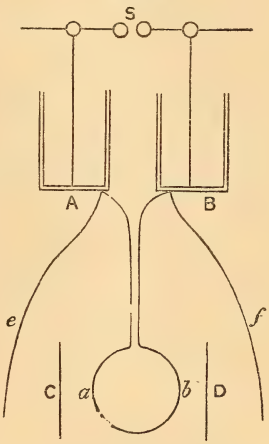


The author repeated this experiment with two Leyden jars arranged as in fig. 1, and found that when the spark-gap was sufficiently large to produce a bright ring when the tinfoil was not connected to earth, doing so produced no noticeable difference in the brilliancy ; but that, if the discharge were faint, it was ren-rendered considerably brighter on making the earth connexion. Better results were, however, obtained on

* Communicated by the Physical Society : read April 28, 1893.
† *Ante*, p. 98.

connecting the tinfoil to either of the outside coatings, A or B, of the jars instead of to earth. This result led the author to try a series of experiments to endeavour to determine the cause of the effect, of which the typical ones are here given.

Fig. 2.



Experiment 1 (*vide* fig. 2). A and B are the outside coatings of a pair of Leyden jars (those employed were about pint size). C and D two vertical and parallel metal plates, at a distance of about one foot from the jars. The spark-gap, S, is adjusted by a screw, so that the spark-length can be varied by small amounts when necessary. A single turn of wire, *a b*, encloses an exhausted bulb, and its ends are connected to A and B, as shown in the figure, so that *a* the part nearest to C is connected to A, and *b* to B. Two loose wires, *e* and *f*, are also connected to A and B.

The spark-gap is now shortened until there is just no luminous ring in the bulb.

The plates C and D are then connected to the outer coatings A and B by means of the two loose wires, with the following results :—

(1) A to C. Bright ring.
(2) B to D. Bright ring.
(3) A to C and B to D simultaneously. Bright ring.
(4) A to D. }
(5) B to C. } No luminous ring.
(6) A to D and B to C. }

Expt. 2.—The wire turn *a b* is removed from the bulb, given a half twist, and then replaced ; so that *a* is now nearest to D, and *b* to C. Plates not connected, no luminous ring.

(1) A to C. }
(2) B to D. } No luminous ring.
(3) A to C and B to D. }
(4) A to D. }
(5) B to C. } Bright ring.
(6) A to D and B to C. }

Expt. 3.—Arranged as in Expt. 1, case (1) or (2). C is then connected to D, and the ring becomes less bright.

Expt. 4.—Arranged as in Expt. 1, case (1). C and D

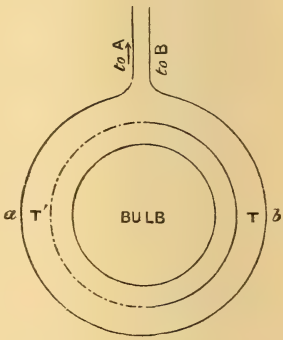
connected. On approaching C to the bulb, ring becomes brighter.

On approaching D less bright.

If arranged as Expt. 1, case (2), the reverse happens.

All the above four experiments give the same effects if the turn of wire be larger than the bulb, as in fig. 3, only a longer spark-gap has to be used.

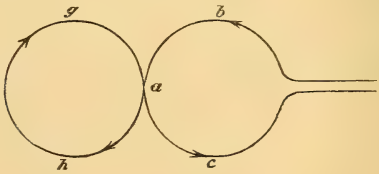
Fig. 3.



Expt. 5.—A single turn of wire (fig. 3), *a b*, larger than the bulb is employed, and between the bulb and the ring a semicircular strip of tinfoil or metal T is placed. The wire is connected as in Expt. 1. The spark-gap is arranged to give no ring. Connecting T to B bright ring, T to A no ring. The reverse happens if the tinfoil is placed in position T′ as shown by the dotted line.

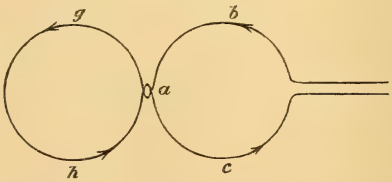
Expt. 6.—A piece of gutta-percha covered wire is bent into shapes shown in figs. 4 and 5. On placing either of these over bulb as in fig. 6, a figure of eight-shaped luminous

Fig. 4.



discharge is obtained, and there is no noticeable difference between the two.

Fig. 5.



Expt. 7.—Putting the wire (fig. 4) on bulb as in fig. 7, a

single broad band-ring is obtained, as the two turns will help one another with respect to magnetizing effect.

Doing the same with the wire (fig. 5) a discharge is obtained shaped like the sector of an orange, as shown by the dotted lines, fig. 7.

Fig. 6.

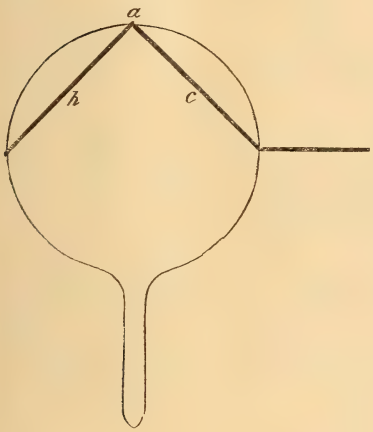
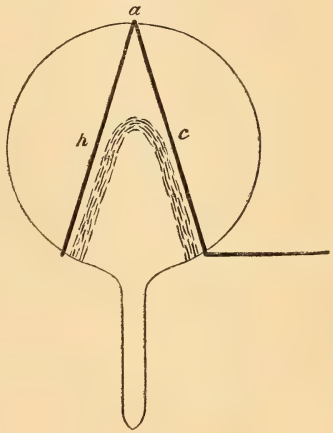
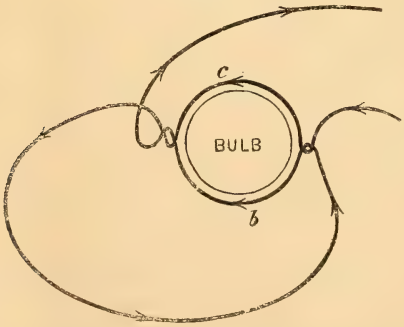


Fig. 7.



Expt. 8.—Bending a wire as shown in fig. 8, and placing a bulb in the loop *b c*, there is no effect even with a long spark-gap, although the potential difference between the sides

Fig. 8.



c and *b* would be much greater than in the case of a single turn.

Putting a bulb in the loop, *b c*, of fig. 4 at once gives a bright ring.

Experiments 6, 7, and 8 seem to show that ring, or other shaped, sharp luminous discharges can only be obtained with the wire so wound as to give magnetic induction through the bulb, while the first five experiments show that an electrostatic field in the bulb may help the effect. The theory the author has come to after consideration of the above and other experiments is :—That if the E.M.F. due to rate of change of magnetic induction acting in the dielectric of rarefied gas be insufficient to break it down and produce a luminous discharge (owing to the spark-gap being too short), the electrostatic field between the plates C and D, or between one of the plates and part of the wire, if correctly timed with respect to the rate of change of current in the wire, will commence the breakdown of the gas, thus allowing a less E.M.F. due to the magnetic induction to complete it.

To put this to the test, a single turn of wire was put round a bulb and the spark-gap adjusted so as to give a very faint or no luminous ring ; on the top of the bulb was laid a piece of tinfoil connected to one pole of a $\frac{1}{4}$ in. spark induction-coil ; when the coil is worked the tube is filled with a faint glow : if now the Leyden jars are charged and discharged there will be sometimes a ring in the bulb which will be occasionally quite bright. The reason it cannot be always bright is of course that the discharges of the induction-coil are periodic, as are also those of the jars, and it is only when the two are properly timed (*i. e.* the P.D. due to the coil coming either just before or simultaneously with the spark) that there will be a bright ring.

This experiment seems to settle the question and show conclusively that a properly timed electric stress in the bulb due to an electrostatic field will allow an E.M.F. due to the alternating current in the wire to produce a breakdown of the rarefied gas, which the latter is too small to effect without the aid of the former*.

In Expt. 1, when A and C are connected this field will exist between C and *b* the side of the turn of wire remote from C, and must therefore pass through the bulb. When A

* To prevent misconception, it had better be definitely stated that this electrostatic stress does not necessarily act in the same direction as the E.M.F. due to the rate of change of magnetic induction. In experiments (1) to (5) the direction of the former will be through the bulb from side to side, while that of the latter is a circle coplanar with the wire. As the discharge in a gas is of a nature more or less electrolytic, being accompanied by the splitting up of the molecules, it seems reasonable to suppose that anything which increases the number of dissociated molecules will enable a smaller stress to produce a breakdown in the form of a luminous discharge.

is connected to D, as the strongest field is between b and D, where the P.D. is greatest, it does not pass through the bulb; in fact the field in the bulb will simply be that due to the P.D. between a and b, or the same as it is if the wires e and f are disconnected. The results of Experiments 2, 3, 4, and 5 are also obviously explained by this theory.

To treat the subject mathematically. We have the well-known equations for the discharge of a condenser:

$$L\frac{dc}{dt} + Rc = -\frac{q}{K}, \text{ where K is the capacity,}$$

and

$$c = \frac{dq}{dt}.$$

Combining these,

$$\frac{d^2q}{dt^2} + \frac{R\,dq}{L\,dt} + \frac{1}{KL}q = 0.$$

To obtain an oscillatory discharge 4L must be greater than KR^2.

Putting a for $-\frac{R}{2L}$ and b for $\sqrt{\frac{1}{KL} - \frac{R^2}{4L^2}}$ the solution is

$$q = Qe^{at}\,\frac{\sqrt{a^2+b^2}}{b}\sin(bt+\theta), \quad . \quad . \quad . \quad (1)$$

where $\theta = \tan^{-1}\left(-\frac{b}{a}\right)$ and Q is the initial charge.

This may be more conveniently written

$$q = Qe^{at}\,\frac{\sqrt{a^2+b^2}}{b}\cos(bt-\eta),$$

where

$$\eta = \frac{\pi}{2} - \theta, \text{ or } \tan\eta = -\frac{a}{b} = \sqrt{\frac{KR^2}{4L-KR^2}}.$$

If the oscillations are to be rapid, $\frac{1}{KL}$ must be large compared to $\frac{R^2}{4L^2}$.

Therefore η will be some small angle.

Instead of quantity we may write P.D. of the condenser, or

$$v = Ve^{at}\,\frac{\sqrt{a^2+b^2}}{b}\cos(bt-\eta). \quad . \quad . \quad . \quad (2)$$

The current

$$c=\frac{dq}{dt}=\frac{Q}{bKL}e^{at}\sin bt=\frac{V}{bL}e^{at}\sin bt. \quad . \quad . \quad . \quad (3)$$

Now the electric stress acting in the bulb is proportional to the rate of change of current, or to $\frac{dc}{dt}$;

and

$$\frac{dc}{dt}=\frac{V}{bL}e^{at}(a\sin bt+b\cos bt). \quad . \quad . \quad . \quad . \quad (4)$$

The current itself will be a maximum or minimum when

$$\frac{dc}{dt}=0;$$

i. e. when

$$a\sin bt+b\cos bt=0,$$

or when

$$\tan bt=-\frac{b}{a}=\sqrt{\frac{4L}{KR^2}-1}.$$

Therefore $bt=\theta$, and is in general nearly equal to $\frac{\pi}{2}$.

The maximum values of the current occur when

$$bt=\theta,\quad 2\pi+\theta,\quad 4\pi+\theta,\ \&c.,$$

and the minimum values when

$$bt=\pi+\theta,\quad 3\pi+\theta,\quad 5\pi+\theta,\ \&c.$$

This is shown in the curve (fig. 9), the points M_1, M_2, M_3, &c., representing the maximum and minimum values of the current. The distance O A represents θ, and $AB=\frac{\pi}{2}-\theta=\eta$.

It is now necessary to consider when the rate of change of the current is greatest. $\frac{dc}{dt}$ will be a maximum or minimum when $\frac{d^2c}{dt^2}=0$.

Now

$$\frac{d^2c}{dt^2}=\frac{V}{bL}e^{at}\{(a^2-b^2)\sin bt+2ab\cos bt\}=0.$$

Hence

$$\tan bt=-\frac{2ab}{a^2-b^2}=-\frac{R\sqrt{K(4L-KR^2)}}{2L-KR^2}.$$

Let

$$\tan^{-1}\frac{R\sqrt{K(4L-KR^2)}}{2L-KR^2}=\gamma.$$

γ will be in general a small angle.

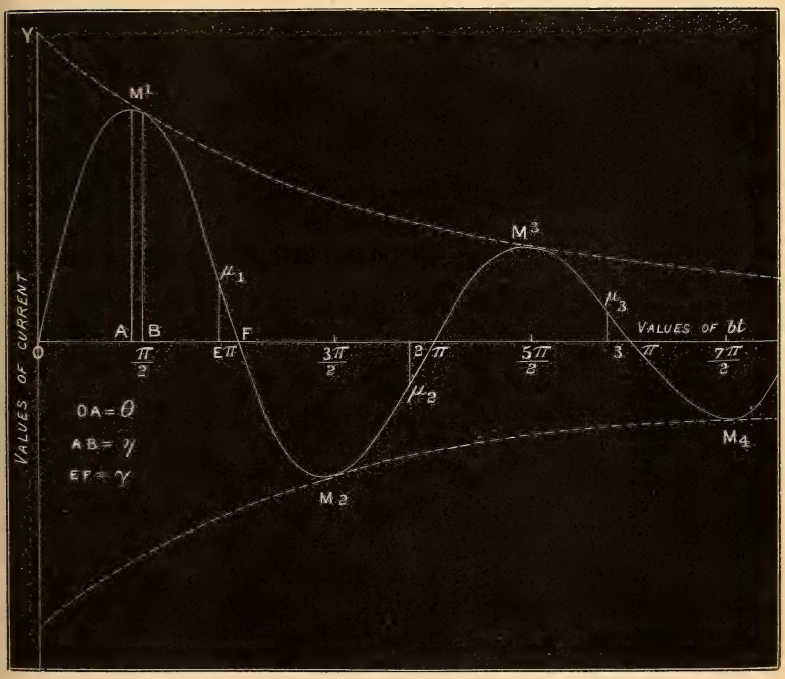
The rate of change of current will be greatest (either a maximum or a minimum) when

$$bt = -\gamma,\ \ \pi-\gamma,\ \ 2\pi-\gamma,\ \&c.$$

Obviously bt cannot equal $-\gamma$, so that the rate of change of current is greatest for values $\pi-\gamma$, $2\pi-\gamma$, &c.; or at points μ_1, μ_2, μ_3, &c. in the curve (fig. 9), and $EF=\gamma$. If

Fig. 9.

Dotted curves are values of the exponential $\frac{V}{bL}e^{-\frac{R}{2L}t}$.



M_1, M_2, M_3, M_4 are the maximum values of the current. μ_1, μ_2, μ_3 are the points where the rate of change of current is greatest.

the oscillations are to be very rapid KR^2 must be negligible compared to $4L$; in which case

$$\tan\gamma = R\sqrt{\frac{K}{L}};$$

also

$$\tan\eta = \frac{R}{2}\sqrt{\frac{K}{L}},$$

and they are both very small angles, hence $\gamma=2\eta$ approximately, or EF=2AB.

When $bt=\pi-\gamma$,

$$\frac{dc}{dt}=\frac{V}{L}e^{-\frac{\pi-\gamma}{\sqrt{\frac{4L}{KR^2}-1}}},$$

or if the oscillations are very rapid,

$$\frac{dc}{dt}=\frac{V}{L}e^{-\frac{\pi R}{2}\sqrt{\frac{K}{L}}}.$$

If, however, $t=0$,

$$\frac{dc}{dt}=\frac{V}{L},$$

so that the greatest rate of change of current occurs at the first instant of discharge, although this is not a mathematical maximum.

Equation (4) may also be written

$$\frac{dc}{dt}=\frac{V\sqrt{a^2+b^2}}{bL}e^{at}\cos(bt+\eta), \quad . \quad . \quad . \quad (5)$$

η being the same angle as before.

It is now necessary to consider the values of the P.D. between the outside coatings A and B of the Leyden jars.

Let l and r be the inductance and resistance of the coil connected to the outer coatings, and L and R the same for the whole circuit. Let $v_1-v_2=x$ be the P.D. between the outer coatings at any instant t. Then

$$c=\frac{V}{bL}e^{at}\sin bt,$$

and

$$x=v_1-v_2=cr+l\frac{dc}{dt},$$

$$\therefore \quad x=\frac{V}{bL}e^{at}\{(r+la)\sin bt+lb\cos bt\}$$

$$=\frac{V}{bL}e^{at}\sqrt{l^2b^2+(r+la)^2}\cos(bt-\eta') \quad . \quad . \quad (6)$$

where

$$\tan\eta'=\frac{\frac{r}{l}+a}{b}.$$

η' will be in general a small angle not very different from η;

and if $\frac{l}{r} = \frac{L}{R}$ or the time-constant of the coil equals the time-constant of the whole circuit,

$$\frac{r}{l} = \frac{R}{L} = -2a,$$

$$\therefore \tan\eta' = -\frac{a}{b} = \tan\eta, \text{ or } \eta' = \eta.$$

That is x is in phase with v the P.D. at the inner coatings of the jars.

To find the maxima and minima of x we have

$$\frac{dx}{dt} = \frac{V}{bL} e^{at} \left[\{ar + l(a^2 - b^2)\} \sin bt + b(r + 2la) \cos bt\right] = 0.$$

$$\therefore \tan bt = -\frac{b(r + 2la)}{ar + l(a^2 - b^2)}$$

$$= \frac{(rL - Rl)\sqrt{K(4L - KR^2)}}{L(KRr + 2L)}$$

$$= \tan\delta.$$

Then x has its greatest positive or negative values when $bt = \delta$, $\pi + \delta$, $2\pi + \delta$, &c. δ is in general a small angle, and is positive if

$$\frac{L}{R} > \frac{l}{r},$$

and negative if

$$\frac{L}{R} < \frac{l}{r}.$$

If

$$\frac{L}{R} = \frac{l}{r}; \quad \delta = 0.$$

If $\frac{L}{R}$ be not greater than $\frac{l}{r}$ the first largest value of x will occur at $t = 0$, and as the rate of change of current is also greatest at this instant the two will occur simultaneously.

The next greatest value of x occurs when

$$bt = \pi - \delta \left(\text{if} \frac{L}{R} < \frac{l}{r}\right),$$

and the next greatest rate of change of current when

$$bt = \pi - \gamma.$$

δ will be less than γ, if $\frac{L}{R}$ be nearly equal to $\frac{l}{r}$; so that the maximum value of x will occur after the maximum of $\frac{dc}{dt}$, but the value of x will not differ very much from its maximum when $\frac{dc}{dt}$ is a maximum*. This bears out the results obtained in experiments 1 and 2, though, of course, the electric field in the bulb will be that due to the P.D. between one of the plates, C or D, and the opposite side of the turn of wire, and this will only be about half that between the outer coatings A and B. Moreover, the phase of the potential of C will not be quite the same as that of A, on account of the inductance of the connecting wire *e*. Experiments 1 and 2 were, however, tried with the plates C and D, and the connecting wires removed, the turn of wire *ab* being moved so as to bring either *a* or *b* nearest to A or to B, and the results obtained were practically the same as those of experiments 1 and 2.

Effect of Size of Jars.

When different-sized Leyden jars are employed with the same length of spark-gap the luminous ring is more brilliant

* The above investigation into the value of the P.D. between the outer coatings will only give correctly the state of things when a steady swing has been set up in the circuit; as evidently when $t=0$ the value of x also equals zero, so that x must start in phase with the current; it will, however, rapidly get out of phase with the latter, and finally be nearly in quadrature with it. This is due to an initial wave starting from the spark-gap which runs round the circuit. Possibly the value of x can be empirically represented by one of the two subjoined formulæ:—

$$x=\frac{Ve^{at}}{bL}\sqrt{l^2b^2+(r+la)^2}\sin\{(bt+\psi)(1-e^{-pt})\},$$

or

$$x=\frac{Ve^{at}}{bL}\sqrt{l^2b^2+(r+la)^2}\sin\{bt+\psi(1-e^{-pt})\},$$

where $\psi=\frac{\pi}{2}-\eta'$, and p some constant. Dr. Lodge, in his researches on the A and B sparks, approximately represents the initial values of x by the current multiplied by the impedance of the conductor r, or makes

$$x=\frac{Ve^{at}}{bL}\sqrt{l^2b^2+r^2}\sin bt.$$

The initial maximum of x will consequently roughly coincide with the maximum of the current, or be near the point M_1 of fig. 9, and will thus come about a quarter of a period before the second maximum rate of change of current, point μ_1 (fig. 9).

with larger jars. Now the E.M.F, acting in the rarefied gas, and producing the breakdown of the same, is proportional to $\frac{dc}{dt}$.

Also the greatest value of $\frac{dc}{dt}$ that first occurs is when $t=0$, and then

$$\frac{dc}{dt}=\frac{V}{L},$$

and the next is for very rapid oscillations

$$\frac{dc}{dt}=\frac{V}{L}e^{-\frac{\pi R}{2}\sqrt{\frac{K}{L}}}.$$

So that the first value of the E.M.F. acting in the gas is independent of the capacity, and the next and succeeding values are less the greater the capacity.

The effect on the eye, however, of the luminous ring will be the time-integral of the discharge or approximately depend on

$$\int_0^\infty \frac{dc}{dt}\,dt.$$

The whole limits of t, viz., from 0 to ∞, cannot be taken at once, as $\frac{dc}{dt}$ keeps reversing, and this reversal will not affect the luminous discharge. Referring to the curve (fig. 9) it will be seen that the first reversal must take place at M_1, when $bt=\theta$, and subsequent ones for values $\pi+\theta$, $2\pi+\theta$, &c., of bt. It is therefore necessary to take first the limits θ and 0, then $\pi+\theta$ and θ; $2\pi+\theta$ and $\pi+\theta$, and so on, alternately writing the integrals plus and minus.

$$\int_0^\infty \frac{dc}{dt}\,.\,dt=\frac{V}{bL}\left\{\Big[e^{at}\sin bt\Big]_0^\theta-\Big[e^{at}\sin bt\Big]_\theta^{\pi+\theta}\right.$$
$$\left.+\Big[e^{at}\sin bt\Big]_{\pi+\theta}^{2\pi+\theta}-\text{\&c. ad inf.}\right\}.$$

Remembering that

$$\sin(\pi+\theta)=-\sin\theta,$$

$$\sin(2\pi+\theta)=\sin\theta,$$

$$\sin(3\pi+\theta)=-\sin\theta, \text{ and so on,}$$

this gives

$$\int_0^\infty \frac{dc}{dt}\cdot dt = \frac{2V}{bL}\sin\theta\left\{e^{\frac{a}{b}\theta} + e^{\frac{a}{b}(\pi+\theta)} + e^{\frac{a}{b}(2\pi+\theta)} + \&c.\right\}.$$

The series in the bracket is a geometrical progression, in which the constant factor is $e^{\frac{a}{b}\pi}$; and, since a is negative, this is less than unity.

Hence

$$\int_0^\infty \frac{dc}{dt}\,dt = \frac{2V\sin\theta}{bL}\cdot\frac{e^{\frac{a}{b}\theta}}{1-e^{\frac{a}{b}\pi}},$$

and

$$\tan\theta = \sqrt{\frac{4L-KR^2}{KR^2}},\ \text{or}\ \sin\theta = \sqrt{\frac{4L-KR^2}{4L}};$$

also

$$b = \sqrt{\frac{4L-KR^2}{4KL^2}},\ \text{and}\ \frac{\sin\theta}{b} = \sqrt{KL};$$

$$\therefore \int_0^\infty \frac{dc}{dt}\,dt = 2V\sqrt{\frac{K}{L}}\cdot\frac{e^{\frac{a}{b}\theta}}{1-e^{\frac{a}{b}\pi}}$$

$$= \frac{2V\sqrt{\frac{K}{L}}}{e^{\theta\sqrt{\frac{KR^2}{4L-KR^2}}} - e^{-(\pi-\theta)\sqrt{\frac{KR^2}{4L-KR^2}}}}.$$

Let $\theta\sqrt{\frac{KR^2}{4L-KR^2}} = x$ and $\pi\sqrt{\frac{KR^2}{4L-KR^2}} = y$.

Then the denominator $= e^x - e^{x-y}$, and

$$e^x = 1 + x + \frac{x^2}{\underline{|2}} + \frac{x^3}{\underline{|3}} + \&c.,$$

$$e^{x-y} = 1 + x - y + \frac{x^2}{\underline{|2}} - \frac{2xy}{\underline{|2}} + \frac{y^2}{\underline{|2}} + \frac{x^3}{\underline{|3}} - \frac{3x^2y}{\underline{|3}} + \frac{3xy^2}{\underline{|3}} - \frac{y^3}{\underline{|3}} + \&c.,$$

$$e^x - e^{x-y} = y + \frac{2xy}{\underline{|2}} - \frac{y^2}{\underline{|2}} + \frac{3x^2y}{\underline{|3}} - \frac{3xy^2}{\underline{|3}} + \frac{y^3}{\underline{|3}}$$

+ terms of the 4th, 5th, &c. powers.

Now x and y will in general be small fractions, since KR^2 is usually much less than 4L.

If the oscillations are very rapid, θ is very nearly equal to $\frac{\pi}{2}$. Hence $y=2x$ approximately. Then e^x-e^{x-y} becomes

$$2x+\frac{2x^3}{6}=2x\left(1+\frac{x^2}{6}\right) \text{ approx.}$$

Therefore the time-integral

$$=\frac{2V\sqrt{\frac{K}{L}}}{2x\left(1+\frac{x^2}{6}\right)}=\frac{V}{x}\sqrt{\frac{K}{L}}\left(1-\frac{x^2}{6}\right) \text{ approx.,}$$

and

$$x=\frac{\pi}{2}\sqrt{\frac{KR^2}{4L-KR^2}}=\frac{\pi R}{4}\sqrt{\frac{K}{L}} \text{ approx.;}$$

so time-integral

$$=\frac{4V}{\pi R}\left(1-\frac{\pi^2R^2K}{96L}\right) \text{ approx.}$$

Now from this it is seen that the effect of increasing the capacity would be to slightly diminish the time-integral, and consequently probably make the brilliancy of the luminous discharge less, if it were not that increasing the capacity diminishes the real resistance of the circuit, since it makes the oscillations slower, and the resistance R for copper for rapid oscillations approximately equals $\sqrt{\frac{1}{2}blR_0}$; where l is the length of the wire, and R_0 its resistance for steady currents. Now $b=\frac{1}{\sqrt{KL}}$ approximately.

Therefore

$$R=\sqrt{\frac{lR_0}{2\sqrt{KL}}};$$

so that the time-integral is very roughly proportional to the fourth root of capacity.

There is also another reason why larger jars might produce a brighter discharge, even though the time-integral were less. With larger jars the time taken for the amplitude of the current to sink to a value at which it becomes insignificant will

be longer than in the case of small ones. Now, as the initial value of $\frac{dc}{dt}$ is the same whatever the size of the jars, the after values (although their time-integral is less and their actual values less also) last longer in the case of larger jars.

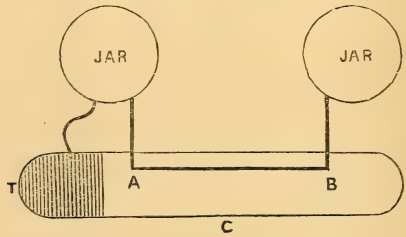
When the breakdown of the dielectric of rarefied gas is once begun by the initial $\frac{dc}{dt}$, the values of $\frac{dc}{dt}$ necessary to keep it up may probably be very much less, and consequently the smaller values of $\frac{dc}{dt}$ lasting longer, as given by the larger jars, may produce a luminous discharge more brilliant to the eye than the larger values of $\frac{dc}{dt}$ lasting a shorter time, as given by the smaller jars.

The actual results obtained with a ring of four turns of wire containing an exhausted bulb about $2\frac{1}{2}$ inches in diameter were that the differences in brilliancy, obtained by using half-gallon jars, pint jars, or very small jars made from specimen glasses, were not so very great.

Other Effects. Apparently unclosed Discharges.

A closed luminous discharge is not the only one that can be obtained. Mr. Tesla, in 1891, pointed out that by wrapping a wire round an exhausted tube so as to form a coarse-pitched spiral, a luminous spiral discharge is obtained. He was apparently only able to obtain a very feebly luminous spiral, but the author has succeeded in getting one quite as brilliant as in the case of the ring-shaped discharge obtained with a bulb.

Fig. 10.



In fig. 10 two half-gallon jars have their outer coatings connected by a wire, A B, bent as shown in the figure. Over

the wire is laid an exhausted tube, C, with a tinfoil cap*, T, at one end; T is connected to the outer coating of the jar nearest to it. The object of this is to utilize the electrostatic effect and make the tube more sensitive to breakdown by the electromagnetic one. When the jars discharge, a straight luminous band is observed in the tube directly over A B.

If the tube C be now moved towards the jars, even by a very small amount, a closed circuit discharge will be obtained. There is apparently, then, a tendency for the luminous discharge to form a closed circuit whenever possible; and it seems probable that even when the discharge is apparently not closed, as in the case of the spiral or the straight line, the electric stress acting in the rarefied gas takes the form of a closed circuit, but is only intense enough to produce sharp luminosity close to the wire†. To further test the question an unclosed ring tube was made, and when it was placed inside a coil of wire no trace of a single luminous band could be seen‡. A small glass tube was also bent so as to form a spiral of four turns, and exhausted. A wire following the spiral was attached to it, but this also gave no trace of luminous discharge.

Magnetic Effects of Discharge.

The ring discharge in a bulb or closed circular tube acts like a metallic circuit as far as magnetic effects are concerned. This may easily be shown by the following experiment.

A coil of three or four turns of wire has a similar one wound with it to form a secondary; the latter is connected to a third coil, in which is placed an exhausted bulb. The first coil is connected to the outside coatings of the jars (fig. 1). The spark-gap can be adjusted so that a fairly bright ring is

* It is not always necessary to use this cap, as, if the exhaustion is high enough to give green phosphorescence of the glass, with the two half-gallon jars in series, the discharge can be obtained without the cap. With another tube of lower vacuum the author finds the cap necessary.

† That is, the return part of the discharge is so diffused and feebly luminous as to easily pass unnoticed in comparison with the sharp and brilliant luminosity close over the conductor. The same applies to the spiral discharge, each turn of the spiral probably forming a closed circuit by itself.

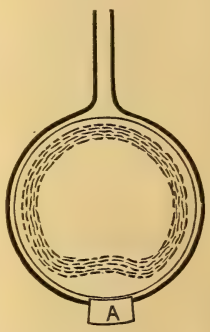
‡ On afterwards repeating this experiment the author obtained a discharge in parts of the tube, and with half-gallon jars in the whole tube. The discharge, however, was a closed one, as there were two distinct bands in the tube, one on the side next to the coil and the other on the side farthest away from it. This is what might be expected if the magnetic induction be sufficiently strong.

produced in the bulb. If now a second bulb is placed within the first coil a luminous ring will be formed in it, and the ring in the other bulb will be much weakened or altogether extinguished. Exactly the same effect is produced if a metal plate or closed coil be brought near the first coil in lieu of the bulb.

Sensitive State of Discharge.

If a single turn of insulated wire surround one of the exhausted bulbs as in fig. 1, and the spark-gap be adjusted so as to produce a rather faint luminous ring (the fainter the better); on approaching the finger and touching the wire at any point the discharge appears to be repelled, and takes the shape shown in fig. 11. Instead of touching the wire with the finger a small piece of tinfoil may be laid between the wire and the bulb, as at A (fig. 11), and this may be touched by the finger or connected to any large object, insulated or otherwise; the effect produced is the same. Connecting the tinfoil to one of the outer coatings of the jars does not produce this effect, and it is scarcely, if at all, visible when the luminous ring is brilliant, due to a longer spark-gap. With a wire ring of several turns the author has not been able to obtain it. If a turn of bare wire be employed the effect is produced when the finger is brought very near to the wire, but if it be brought into actual contact the effect is no longer visible. This apparently shows that it is due to the capacity between the finger or tinfoil and the wire; it is probably of the same nature as the "sensitive state" in an ordinary vacuum tube.

Fig. 11.



ADDENDUM, May 1st, 1893.

Since writing the above the author has made a further experiment* which at first sight appears to contradict the one† given in the paragraph on "Magnetic Effects of Discharge."

* Called hereafter the second experiment. This experiment was shown when the paper was read.

† Called hereafter the first experiment.

A ring (R) of four turns of wire is joined in series with a single turn, and the two are connected to the outside coatings of the jars. In the single turn a bulb is placed and the spark-gap adjusted until a fairly bright ring is produced in it at every discharge. If now a closed ring of thick copper-wire, a metal plate, or a ring of several turns, similar to R, and with its ends joined, be laid on R to act as a secondary, the luminous ring in the bulb is brighter ; on substituting for this an exhausted bulb and placing it in R, there will be a brilliant ring-discharge in it, while the discharge in the other bulb will be rendered fainter or altogether extinguished. In this experiment the exhausted bulb secondary appears to act in the reverse way to a metallic secondary.

The author then made the following experiments :—

(*a*) A ring of four turns of guttapercha-covered wire precisely similar to R was made, its ends were connected to an ordinary Geissler tube. When this was used as secondary it acted exactly in the same manner as the exhausted bulb both in the first and second experiments, the Geissler tube being brilliantly illuminated.

(*b*) The Geissler tube was then removed, and the ends of the secondary coil connected to the coatings of a small Leyden jar. The effects produced by this secondary were the same as those produced by the exhausted bulb in both experiments.

(*c*) The ends of the secondary were connected to the loops of a glow-lamp to act as a resistance (about 100 ohms). This acted similarly to the exhausted bulb in both experiments.

(*d*) A disk of gilt paper (imitation) and also a ring of the same were used as secondaries ; these acted similarly to the bulb in both experiments. When the discharge took place there were brilliant sparks produced at various spots on the paper, wherever there was any flaw in the gilding, showing that considerable energy was dissipated there.

(*e*) The secondary coil of four turns had its ends joined by a strip of gilt paper about 6 inches in length, with a considerable number of flaws in the gilding (produced purposely, by bending the paper sharply in several places, so as to obtain considerable sparking). This acted similarly to the bulb and dimmed the discharge in the bulb surrounded by the single turn. On shortening the length of gilt paper between the ends of the secondary, the discharge in the bulb was less dimmed.

The results of these five experiments are, that any of the above secondaries are able to reduce the mutual induction between the primary and secondary in the first experiment sufficiently to render faint or altogether extinguish the

discharge in the bulb, and act similarly to an exhausted bulb secondary. In the second experiment a low resistance secondary behaves in the reverse manner to an exhausted bulb secondary, while (*c*) and (*e*) show that a high resistance put externally into the secondary circuit, and (*d*) that a secondary having a high resistance in itself, act in a similar manner to an exhausted bulb secondary. (*b*) shows that if the ends of the secondary be attached to a capacity it behaves like the bulb.

The most probable explanation seems to be the following:—The amount of energy in the jars when charged is a fixed quantity for a given spark-gap; this energy will be mostly expended in the coil R and the single turn and bulb (the second experiment). If, now, we can make energy be expended elsewhere, as in a secondary, we shall have diminished the energy received by the bulb, and this will in general dim it or altogether extinguish it. This will explain what happens when an exhausted bulb secondary is used; also experiments (*a*), (*c*), (*d*), and (*e*). With regard to experiment (*b*), energy may have been expended in heating the glass of the jar on account of electric hysteresis. Moreover, this secondary did not dim the bulb so much as the others, but was found to be capable of improvement in this respect by including some resistance (in the shape of the glow-lamp or a strip of gilt paper) in its circuit.

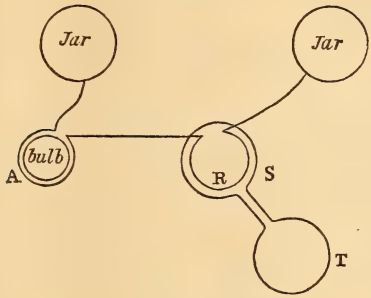
In the case of a low-resistance secondary the energy dissipated in it will be small, since its impedance will not be much lessened by its being of low resistance on account of the high frequency. This does not explain, however, why the discharge in the bulb is brighter when a low-resistance secondary is used*.

A further experiment was then made. The coil R in the second experiment had a similar secondary S placed in it; this was connected to another similar coil T. The spark-gap was lengthened until a brilliant luminous ring was produced in a bulb placed in T. The bulb in A was then moved away from A until there was a very faint luminous ring in it. On removing the bulb from T a very slight brightening of the

* This energy explanation is probably not a complete one. Working out the frequency in the cases of no secondary, a secondary of four turns short-circuited, and the same with its ends joined through 100^{ω}; the author finds that the damping-term is increased when either secondary is used, but more so with the 100^{ω} in circuit. The frequency is much the same with the 100^{ω} in circuit as when there is no secondary, but with the secondary short-circuited the frequency is about doubled. This may account for the increase in brightness of the discharge in the bulb.

faint ring of the bulb in A was observed. Instead of placing an exhausted bulb in T, a coil of four turns with its ends joined through 100 was laid on T, and the bulb in A adjusted

Fig. 12.



A one turn; S, R, and T each four turns.

to give a very faint ring; on removing the coil from T a decided brightening of the discharge in the bulb was observed. This experiment seems to show fairly conclusively that increasing the energy in the circuit of the secondary S diminishes the brightness of the discharge in the bulb placed in A*.

LIII. *Comparative Experiments with the Dry- and Wet-Bulb Psychrometer and an improved Chemical Hygrometer.* By M. S. Pembrey, *M.A., M.B., Radcliffe Travelling Fellow; late Fell Exhibitioner of Christ Church, Oxford.* (*From the Radcliffe Observatory, Oxford.*)†

During the late winter it seemed desirable to make a series of comparative experiments with the Dry- and Wet-Bulb Psychrometer and an improved Chemical Hygrometer, in order to ascertain the accuracy of the results given by the Psychrometer for temperatures below the freezing-point.

A series of comparative experiments, made by me in the summer of 1889, had shown that the amounts of moisture calculated from the psychrometric readings varied by +6 per cent. to −5 per cent. from the amounts actually found by the

* Since writing the above the author finds that Prof. J. J. Thomson has observed the effects noticed in the second experiment, and gives an explanation practically identical with the above.

† Communicated by Mr. E. J. Stone, F.R.S., Radcliffe Observer.

chemical method. The mean difference, however, in the above series was insensible*.

The Chemical Hygrometer employed in both series was that introduced by Dr. Haldane and the author†.

The absorption-tubes were placed in a small wooden box with wire partitions to prevent them from knocking against each other. The entrance-tube, by which the air to be examined passed into the hygrometer, was fixed through a small perforation in a rubber partition covering a hole in the box. In this way any possibility of air being taken from the inside of the box was avoided.

The comparative experiments were made in the following manner. The weighed absorption-tubes were placed in the shed containing the psychrometer about ten inches below the bulbs of the thermometers. The wet- and dry-bulbs were then read off; the absorption-tubes were connected by a long piece of rubber-tubing with the aspirator. Air was now drawn through the tubes at a rate of 1500 cub. centim. per minute, until about 11,500 cub. centim. of the air had been taken. Five readings of the temperature of the water and of the air in the aspirator were taken during each period of observation. When the aspiration was finished, the readings of the wet- and dry-bulbs were again taken, and the absorption-tubes disconnected and stoppered. The period of observation generally lasted about ten minutes.

Simultaneous determinations with two chemical hygrometers were made in the previous, but not in the present series of observations. In order, however, to check the completeness of the absorption and any errors in weighing, a second pair of absorption-tubes was connected up with the first pair.

The results for the psychrometer were calculated, not from my own readings, but from the mean of three other readings —one at the beginning, one at the middle, and one at the end of each period of aspiration. These readings were obtained from the continuous photographic record of the wet- and dry-bulbs taken at the Radcliffe Observatory. It is possible to read off this record to two minutes and to one-tenth of a degree Fahrenheit. The accuracy of the readings has been proved by years of use and comparison with eye-readings.

In every case care was taken to have the wet-bulb properly moistened about a quarter of an hour before the observations.

* Phil. Mag. April 1890, p. 314.

† "An Improved Method of Determining Moisture and Carbonic Acid in Air." Haldane and Pembrey, Phil. Mag. April 1890.

TABLE I.

Experiment.	Date.	Time during which air was aspirated through absorption-tubes.	Corrected volume of air aspirated.	Gain in weight of absorption-tubes, first pair.	Variation in weight of test-pair of absorption-tubes.	Weight of vapour calculated from psychrometer by Glaisher's Tables.	Percentage difference of psychrometer over chemical method.	Dry-bulb (mean of three readings).	Wet-bulb (mean of three readings).
			cub. centim.	grm.	grm.	grm.	per cent.	° F.	°
1.	3 Jan. 1893.	2.26 – 2.31 P.M.	5,802	·0209	+·0002	·0198	−5	31·1	29·0
2.	4 „	10.15 –10.19½ A.M.	5,630	·0154	+·0002	·0164	+7	20·1	20·0
3.	5 „	10.4½ –10.14 „	11,552	·0289	+·0003	·0288	−0	20·0	19·6
4.	„ „	10.41 –10.51 „	11,278	·0303	+·0001	·0297	−2	21·0	20·5
5.	6 „	10.20 –10.29 „	11,358	·0445	+·0001	·0470	+5	30·7	29·9
6.	„ „	11.2½ –11.12 „	11,396	·0481	−·0002	·0480	−0	30·9	30·4
7.	7 „	10.45 –10.54 „	11,174	·0431	+·0005	·0427	−1	28·6	28·1
8.	„ „	11.21½–11.33 „	11,202	·0439	+·0002	·0448	+2	28·5	28·2
9.	9 „	10.14 –10.23 „	11,302	·0576	−·0002	·0589	+2	34·1	33·8
10.	„ „	10.45 –10.54 „	11,320	·0587	+·0003	·0583	−0	34·3	33·9
11.	10 „	10·7 –10.16 „	11,370	·0574	+·0004	·0575	+0	34·7	34·2
12.	„ „	10.39 –10.48 „	11,410	·0578	+·0001	·0603	+4	35·2	34·7
13.	11 „	10.14 –10.23 „	11,428	·0481	+·0002	·0476	−1	32·3	30·9

The aspirator used was that described in the paper previously mentioned*. The aspirating-bottles were covered with felt, so that the temperature of the water generally varied only a tenth or two of a degree Centigrade, never more than half a degree, during the period of observation.

The volume of air aspirated has always been corrected for temperature, aqueous vapour, and barometric height.

In calculating the tension of aqueous vapour from the chemical determinations the table given by Shaw† has proved very valuable.

The preceding Table (I.) shows that the amounts of moisture calculated from the psychrometric readings by Glaisher's Tables vary, when compared with the gravimetric determinations, from −5 per cent. to +7 per cent. The mean, however, is ·0430 to ·0426 grm., or less than +1 per cent. for the psychrometer.

The tensions given by the chemical determinations have been calculated, and are compared in Table II. with those obtained from the psychrometer by means of Glaisher's, Haeghens', Guyot's, and Wild's tables.

TABLE II.

Experiment.	Chemical method.	Psychrometer.			
		Glaisher.	Haeghens.	Guyot.	Wild.
	millim.	millim.	millim.	millim.	millim.
1.	3·45	3·20	3·44	3·45	3·47
2.	2·60	2·67	2·73	2·72	2·73
3.	2·49	2·36	2·58	2·56	2·57
4.	2·56	2·36	2·70	2·64	2·61
5.	3·75	3·83	4·01	3·98	3·93
6.	4·03	4·06	4·20	4·16	4·11
7.	3·70	3·63	3·80	3·78	3·73
8.	3·75	3·78	3·84	3·81	3·83
9.	4·87	4·85	4·84	4·82	4·83
10.	4·95	4·85	4·84	4·82	4·80
11.	4·85	4·87	4·86	4·82	4·80
12.	4·86	4·98	4·97	4·92	5·00
13.	4·05	3·86	4·23	3·96	4·17
Mean	3·84	3·80	3·93	3·88	3·89

In order to make this paper more complete, the corresponding tables of the previous experiments are here reproduced.

* Phil. Mag. April 1890, p. 309.

† "On Hygrometric Methods," Phil. Trans. 1888. A.

TABLE III.

Experiment.	Date.	Time during which air was aspirated.	Corrected volume of air aspirated through each pair.	Gain in weight of pair 1, determination A.	Gain in weight of pair 2, determination B.	Weight of vapour calculated from readings of psychrometer by Glaisher's Tables, 7th ed.	Percentage difference of pyschrometer over chemical method.	Dry-bulb (mean of 3 readings).	Wet-bulb (mean of 3 readings).	Variations of test pair 3, showing that carrying the tubes about introduced no error of weighing.
			cub. centim.	grm.	grm.	grm.	per cent.	° F.	°	grm.
1.	16 July 1889.	11.39–11.48 A.M.	5723	·0421	·0430*	·0450	+5½	61·6	53·0	+·0001
2.	17 „	11.39–11.45 A.M.	5722	·0529	·0524	·0552	+5	58·3	54·5	+·0002
3.	18 „	11.10–11.16 A.M.	5723	·0516	·0512	·0520	+1	61·3	54·9	−·0002
4.	19 „	11.6 –11.12 A.M.	5780	·0502	·0508	·0519	+3	63·7	56·0	+·0002
5.	20 „	11.45–11.52 A.M.	5681	·0613	·0610	·0600	−2	57·9	56·0	+·0003
6.	22 „	12.13–12.16 P.M.	5732	·0440	·0435	·0452	+3	61·5	53·0	−·0002
7.	5 Aug. 1889.	11.52–11.58 A.M.	5707	.....	·0687	·0668	−3	65·6	60·7	−·0003
8.	6 „	11.48–11.54 A.M.	5709	.....	·0564	·0548	−3	62·5	56·5	±·0000
9.	7 „	11.21–11.27 A.M.	5756	·0510	·0510	·0495	−3	63·0	55·2	+·0002
10.	8 „	11.0 –11.7 A.M.	5776	·0575	·0572	·0552	−4	64·1	57·0	+·0001
11.	9 „	11.24–11.30 A.M.	5731	·0678	·0675	·0678	±0	61·0	58·9	+·0002
12.	10 „	11.32–11.39 A.M.	5755	·0583	·0585	·0553	−5	64·6	57·4	−·0001

* The rubber of one of the stoppers was found to be split on reaching the Observatory, and this accounts for the slight excess in weight of this pair of tubes.

TABLE IV.

Experiment.	Chemical method.	Psychrometer.			
		Glaisher.	Haeghens.	Guyot.	Wild.
	millim.	millim.	millim.	millim.	millim.
1.	7·43	7·76	7·37	7·31	7·4
2.	9·15	9·55	9·54	9·51	9·5
3.	8·99	9·00	8·88	8·87	8·9
4.	8·78	8·99	8·74	8·77	8·8
5.	10·70	10·72	10·75	10·76	10·7
6.	7·63	7·78	7·39	7·34	7·4
7.	12·15	11·72	11·78	11·80	11·7
8.	9·91	9·65	9·57	9·57	9·6
9.	8·90	8·68	8·45	8·43	8·5
10.	10·00	9·52	9·38	9·41	9·4
11.	11·82	11·84	11·93	11·93	11·9
12.	10·23	9·67	9·55	9·57	9·5
Mean	9·64	9·57	9·44	9·44	9·44

Regnault*, during his comparative experiments with the psychrometer and his chemical hygrometer, made a series of determinations in which the temperature of the air was below the freezing-point. The experiments were made in December 1846 and January 1847. The lowest temperatures during the sixteen determinations were $-6°{\cdot}89$ C. for the dry-bulb and $-7°{\cdot}74$ for the wet-bulb; the highest $-0°{\cdot}13$ and $-0°{\cdot}69$ respectively. The chemical determination lasted from three-quarters of an hour to one hour; readings of the psychrometer were taken every five minutes.

The results showed variations of the psychrometer over the chemical method ranging from $+11$ per cent. to -3 per cent., the mean being about $+4$ per cent.

In conclusion I must express my hearty thanks to Mr. Stone, the Radcliffe Observer, who has given me every facility to make these and the previous experiments, and has always aided me with his advice. I must also thank his assistants, Messrs. Wickham, Robinson, and Maclean.

* *Annales de Chimie et de Physique*, t. xxxvii. 1853, p. 274.

LIV. *Water as a Catalyst.* *By* R. E. Hughes, *B.A., B.Sc., F.C.S., late Scholar of Jesus College, Oxford, Natural Science Master, Eastbourne College* *.

SOME further chemical changes have been investigated, and the influence of the absence or presence of water on the progress of the change has been determined. Last year the author showed (Phil. Mag. xxxiii. p. 471) that dried hydrogen-sulphide gas has no action on the dried salts of lead, cadmium, arsenic, &c.; and, in conjunction with Mr. F. Wilson, it was shown that dried hydrogen-chloride gas is without action on calcium or barium carbonates (Phil. Mag. xxxiv. p. 117).

Silver chloride prepared in the dark, dried perfectly in an air-bath, and then placed on a watch-glass in a desiccator partially exhausted, was found to be not perceptibly darkened in sunlight even after an exposure of some hours; whereas a rapid darkening takes place if moisture is introduced.

It is a well-known fact that paper, especially ordinary glazed writing-paper, when moistened with a solution of potassium iodide and exposed to the light, becomes of a brownish-violet tint—due doubtless to the decomposition of the KI and liberation of the iodine.

The author finds that the progress of this change is subject to several conditions. A solution of potassium iodide placed on glass or porcelain becomes brown only after an exposure of some days. This change, it is suggested, is due to either the organic matter or the ozone in the atmosphere.

A piece of ordinary filter-paper soaked with a saturated solution of KI was dried in the dark. When placed on a watch-glass under a desiccator, no change took place on exposure even after some days; although crystals of the salt were formed on the paper. Moreover, generally speaking, the wetter the paper the deeper was the tint produced. In fact the tint was proportional to the quantity of water present. When no water was present, then no change took place. Further, a strip of filter-paper floated on the top of a solution of KI for quite two hours in bright sunlight before any perceptible darkening occurred, although the underside had assumed a deep brown tint.

But this change also depends on the kind of paper used;

* Communicated by the Author. [As some of Mr. Hughes' results have been anticipated by Mr. Baker (Proc. Chem. Soc. May 4, 1893, p. 129), he wishes it to be stated that the MS. was received by us on April 21st.—Eds.]

thus strips of highly glazed note-paper, ordinary filter-paper, Swedish filter-paper, and vegetable parchment were cut, soaked in the same KI solution, and exposed side by side to bright sunlight. It was found that after some hours a gradation of tints was thus obtained, the deepest being that on the glazed paper, whereas the tint of the parchment was almost imperceptible. Hence this change is perhaps due to the traces of chlorine invariably present in glazed paper. The depth of tint in the same paper was affected by the surface on which the paper lies. Thus, if lying on blotting-paper the change was very minute, slightly more perceptible on glass or polished surfaces, and most evident when on wood or other rough surface. This chemical decomposition also took place in the dark but more slowly; further, once the paper was quite dry, no perceptible deepening in tint was observed. A solution of potassium iodide may be kept in sunlight for an indefinite period, provided it is not exposed to the atmosphere. This change is doubtless due to organic matter or ozone present in the atmosphere, but is dependent on the presence of moisture; whereas the staining of paper by this solution is due to the chlorine present or other constituent of the glaze, and is also dependent on the presence of moisture.

Silver nitrate behaves closely similarly, as also to a lesser degree does platinum chloride.

Some experiments were then made to determine the question whether dried hydrochloric-acid gas has any action on dry silver nitrate.

The gas was passed through a tube containing copper filings (to remove chlorine), then through a series of drying-tubes containing strong H_2SO_4, and finally over P_2O_5 contained in a tube. This dried gas had no action on dried blue litmus-paper. The silver nitrate was contained in a porcelain boat, and had been previously heated to incipient fusion. The gas was allowed to pass slowly through for about two hours. A very slight change of colour was produced in the silver salt, and a slight change *did* take place. By weighing before and after, the amount of change was determined and found to be 1·7 per cent. of the theoretical amount of change. This experiment was conducted at the temperature of the laboratory. An experiment conducted at 100° showed that 1·0 per cent. of the theoretical amount of change had taken place.

The action of dried HCl gas on dried manganese dioxide was next investigated. This MnO_2 was prepared from a pure manganous sulphate by treatment with bromine and caustic soda. It was thoroughly washed and dried.

In this instance a decided change undoubtedly takes place, which appears to be totally independent of the absence or presence of water. In one experiment the change observed was 20 per cent. of the theoretical amount, this particular experiment being conducted at the temperature of the laboratory. In an experiment conducted at 100° the change was 13 per cent., whereas in another experiment conducted at the ordinary temperature, as much as 42·7 per cent. of the theoretical amount of change took place. In all these experiments the gas was allowed to pass for about three hours.

Experiments of a different character were then undertaken.

An "inactive" solvent, such as anhydrous ether in one case and benzene in another, was taken, and silver nitrate dissolved in it by warming. Through the solution a current of dried HCl gas was passed.

For some time no change could be observed, and even after one hour only a very slight turbidity was produced.

Using absolute alcohol as the solvent, a more decided precipitate was obtained at the end of one hour; but the change was still only very partial, as was shown by the remarkable increase in the precipitate on the addition of a minute quantity of water.

Mercuric chloride was dissolved in absolute alcohol, and through this solution a current of dried hydrogen sulphide gas (dried according to the method described in Phil. Mag. xxxiii. p. 471) was passed. For about a quarter of an hour or even longer no change was noticed, then a slight turbidity which became more perceptible, very slowly assuming a pale yellow colour, then a darker yellow, and finally a greenish yellow precipitate was obtained. No further change was observed even after one hour and a half—the change is in fact a limited one, and the green insoluble compound produced is doubtless a double chloride and sulphide of mercury.

The addition of a little water instantly changed this green precipitate to a black one. It is intended to repeat these experiments quantitatively.

An experiment was conducted to determine whether dried HCl gas and dried ammonia gas combine when mixed.

The method was as follows:—Two equally-sized U-shaped glass tubes, with their limbs sealed, and having narrow side delivery-tubes capable of being drawn out and sealed, were taken. One of these tubes, in the bend of which was placed some freshly heated lime, was filled with dried ammonia gas and sealed. The other tube, containing phosphorous pentoxide in the bend, was filled with dried hydrochloric-acid gas,

and the side tube similarly drawn out and sealed. These two tubes were then allowed to stand for three days. The drawn-out ends were then joined by a piece of india-rubber tubing, previously soaked in melted paraffin, and the ends broken off.

The contents of the two tubes being thus placed in connexion with each other, were allowed to remain so for 24 hours.

No deposition of a solid on the clean sides of either tube was noticed. On passing a current of air through the two tubes the contents were driven out, a white fume being evident, however, only on the mixed gases reaching the outside air, while simultaneously a strong odour of ammonia was perceptible.

A similarly conducted experiment gave a similar result, so that it seems certain that dried HCl and dried NH_3 when mixed do not combine.

Eastbourne College.

LV. *Notices respecting New Books.*

Alternating Currents. By Frederick Bedell, *Ph.D., and* Albert C. Crehore, *Ph.D., of Cornell University.* (Whittaker and Co.)

PART I., of 207 pages, is an analytical treatment of the subject, and Part II., of 104 pages, is graphical.

The book is intended for students and engineers. Self-induction is regarded as constant and nothing is said of mutual induction between circuits. The transformer is not touched upon. Simple harmonic functions of the time are dealt with almost exclusively, but there are two short references to periodic functions in general. In Part II. the same problems are considered in the same order as in Part I.

The first eleven chapters, of 175 pages, deal with the following problem:—Given e the electromotive force in a circuit, of resistance R, self-induction L, and containing a condenser of capacity C, to find i the current. The solution of this problem for all cases may be given in one page or in a thousand, depending upon the previous knowledge of the reader. The authors of this book seem at some places to assume a considerable amount of mathematical knowledge; where, as in chapters iii. and v. for example, they discuss very unnecessarily the conditions for $Pdx+Qdy+Sdz$ being a complete differential. At other places, however, the whole working-out of an easy integral is given, seeming to be copied from a beginner's rough note-book. Regarded as exercise-work on the application of the Calculus to alternating current problems,

the book may be recommended to beginners, particularly as some numerical exercises are given, and some curves are given to illustrate the answers; and the most general case is led up to gradually. We feel, however, that the authors have not taken advantage of their good opportunity. Surely it would have been better to begin by showing the student that in most practical problems d/dt enters in a linear fashion, and if we indicate it by θ this symbol may be used like an algebraic quantity. Self-induction means a resistance $L\theta$; a condenser is represented by a resistance $1/C\theta$; and the problem of these eleven chapters is to find

$$e \div \left(R + L\theta + \frac{1}{C\theta} \right).$$

We are sorry to think that the authors mention so very few of the interesting exercises which may be given to students on this subject.

Chapters xii. and xiii. are devoted to a subject which is rather remote from the previous one; it is one on which they seem to have written original scientific papers,—"circuits containing distributed capacity and self-induction." It is unfortunate that a very serious mistake should be made at the beginning. The mistake leads to the equation

$$\frac{d^2e}{dx^2} + LC\frac{d^2e}{dt^2} - RC\frac{de}{dt} = 0.$$

Now a very little consideration ought to have shown the authors that the self-induction term must be of the same sign as the resistance term. If they had used the symbolical method already referred to, they must have seen that they had only to use $R + L\theta$, instead of R in the equation as given by Lord Kelvin originally. We have no time to investigate the amount of error which is introduced by this negative self-induction into the results of the authors, nor even to test their results by those given by Mr. Heaviside (Phil. Mag. January 1887).

In Part II. there is no attempt to give new matter; students who care for the graphical treatment of this subject will find it sufficiently easy to understand.

Discussion of the Precision of Measurements, with Examples taken mainly from Physics and Electrical Engineering. By SILAS W. HOLMAN, *S.B.* (176 pages). (Kegan Paul, Trench, Trübner, & Co., Limited.)

WE understand that this is a publication of Prof. Holman's notes of a regular course of lectures delivered by him at the Massachusetts Institute of Technology. What is the probable accuracy of an experimental result? What accuracy is essential? How

may a sufficiently accurate result be obtained with the least trouble? All experimenters ask themselves these questions, and often answer in an off-hand, unscientific way. Prof. Holman is impressed with the importance of establishing a course of procedure easily understood and fairly general, and not too laborious in its application. As he says in his preface:—"In venturing to urge the importance of the subject as a course of study for engineers and for students of physics, or other pure sciences, the author would suggest the value of the attitude of mind produced by it. One who has in any reasonable degree mastered its methods, although he may never apply them directly, will not only have increased his power to intelligently scrutinize experimental results, but will have acquired a tendency to do so. And it is, perhaps, not too much to hope that he may acquire a notion of a judicious distribution of effort which, with the best of results to himself, he may carry into quite other matters." The course of procedure seems to us to be one which is practised by every experienced laboratory worker, and whether one ought to adopt it instinctively and because it is natural to exercise some common sense even in a physical laboratory, or whether the inexperienced laboratory worker should study it by listening to lectures on it as a new science are questions which Prof. Holman's old pupils can best answer. An experienced man who already follows the course of procedure will, we think, read the book with greater pleasure and benefit than the students for whom it has been written. In the planning of direct measurement the method of procedure is summarized as follows:—

(*a*) Obtain a general idea of the proposed method, apparatus, and conditions of work, or of several methods, &c., from which selection may be made.

(*b*) Make a thorough study of all discoverable sources of error, taking preliminary observations if necessary.

(*c*) Plan the sufficient removal of all determinate sources of error or determine corrections for them.

(*d*) Take the final series of observations.

Of course this summary gives only a one-sided view of the teaching, but still the book is intended to be read by students who need to be taught these things. We should have thought that work in the laboratory and attendance at a few meetings of a Scientific Society would have better effected the author's purpose. We can hardly forgive the author for ignoring altogether the use of squared paper by experimenters.

Prof. Holman would, probably, deliver an interesting course of lectures to babies to teach them how to walk; but after all the babies will learn better through falling and crawling and general experience. So a student will learn more in a good laboratory, under an experienced demonstrator, than from this course of lectures. It is the experienced demonstrator who will enjoy reading the book.

LVI. *Intelligence and Miscellaneous Articles.*

ON THE DISENGAGEMENT OF HEAT OCCURRING WHEN ELECTRICAL VIBRATIONS ARE TRANSMITTED THROUGH WIRES. BY DR. I. KLEMENČIČ.

THE present research is concerned in the first place with the disengagement of heat which occurs when electrical vibrations are transmitted through wires. For the experimental investigation a method was used which consisted in placing close to the wire to be heated the junction of a thermo-element constructed of fine wires, and measuring the heating of the wire due to the radiation against the junction by the thermo-current produced. The primary circuit furnished waves 3·3 m. in length, and consisted of two brass disks 30 cm. in diameter, which were connected by a linear conductor with a spark-gap in the middle. An exactly similar body constituted the secondary inductor, except that it had no spark-gap, but the middle part of the linear conductor was formed of the wires to be investigated. Two experimental wires were interposed; the length of both together was at most 12 cm., while the whole linear part of the secondary inductors had a length of 89 cm. Experiments on the development of heat in wires led thus to the question of the division of the electrical current in vibrations. With regard to the circumstance that the disengagement of heat in very rapid electrical oscillations takes place almost exclusively in the surface-layer, it seemed to the author not unimportant to observe how in this case the intensity of the radiation is related to the change of resistance of the heated wire, and then further to investigate what is the value of this ratio with constant current. Measurements have shown that with wires of the thickness here examined (0·037 cm.) there is no appreciable difference in this respect. The heat disengaged on the surface is rapidly conducted to the interior of the wire. It follows from the experiments on the disengagement of heat that the resistance to the passage of very rapid electrical vibrations depends on the magnetizability of the wire in question, and on the kind of wire; yet as regards the latter in a way differing from the constant current. For several wires of different material 6 cm. in length and 0·037 cm. in thickness, a heat is found in vibrations which is approximately expressed by the following ratio:—

Iron : german silver : brass : copper = 10·5 : 1·75 : 1 : 1.

The number for copper is probably too large, as it was inserted in the series after a correction which was only approximately correct.

If the formulæ of Stefan are applied to these observations, theory and experiment agree well in the combination german silver-brass. The combination german silver-copper did not give concordant values, which is partially due to the fact that in these experiments all the conditions were not fulfilled which theory requires.

Taking Stefan's formula the number 111 was obtained for the magnetic permeability of iron, and in another 73. The observations

showed further that in the branching of electrical vibrations the coefficient of self-induction is almost entirely of dominant influence and not the resistance.—*Wiener Berichte*, March 16, 1893.

ON THE POTENTIAL OF ELECTRICAL DISCHARGE.

BY PROF. HEYDWEILLER.

The author, at the conclusion of a paper on this subject, gives the following table for the values of the potential of discharge, v, between equal spherical electrodes of radius r, for sparking-distances d cm.; the experiments were made by means of a spark-micrometer of suitable construction, so that no appreciable inductive actions were to be feared. The experiments were made at a pressure of 745 mm. and at a temperature of 18° C.; for an increase of pressure of 8 mm. or for a diminution of temperature of 3°, these values are to be raised 1 per cent. in either case.

$r=2{\cdot}5$ cm.		$r=1{\cdot}0$ cm.	
d cm.	v	d cm.	v.
0·5	61·2	0·1	15·7
0·6	72·0	0·2	27·0
0·7	81·8	0·3	37·9
0·8	91·1	0·4	48·3
0·9	100·3	0·5	58·3
1·0	109·5	0·6	67·9
1·1	118·6	0·7	77·5
1·2	127·7	0·8	86·8
1·3	136·7	1·0	104·3
1·4	145·6	1·2	118·3
1·5	154·1	1·4	128·8
1·6	162·2	1·6	137·6

$r=0{\cdot}5$ cm.		$r=0{\cdot}25$ cm.	
d cm.	v.	d cm.	v.
0·1	16·0	0·1	16·1
0·2	27·9	0·2	27·9
0·3	37·9	0·3	37·8
0·4	48·5	0·4	45·9
0·5	57·7	0·5	52·4
0·6	66·4	0·6	57·3
0·7	73·5	0·7	61·0
0·8	80·3	0·8	63·4
0·9	85·3	1·0	67·3
1·0	90·0	1·5	74·4

With the accuracy of 1 per cent. which these values possess as derived both from Paschen's observations and my own, they will be sufficient in most cases for practical purposes, and will probably have attained the limit of accuracy possible in such cases.—Wiedemann's *Annalen*, xlviii. p. 213, 1893.

ON A PROPERTY OF THE ANODES OF GEISSLER'S TUBES.

BY E. GOLDSTEIN.

While a great number of properties of the kathode of induced discharges in rarefied spaces have been made out, only a few properties of anodes are known. The following communication describes a new property of the anode. If a vessel in which the discharge takes place, one for instance with electrodes at the ends

opposite each other, exceeds a certain width, as the rarefaction proceeds the positive light, if it does not wholly disappear, is reduced to a thin layer on the surface of the anode, and the anode "glows." In rarefied air, which is assumed to be the medium of these experiments, the colour is peach-blossom. If an electrode is made of pieces of different metals, for instance if a disk is used half of aluminium and half of silver, the kathode light is generally distributed over both halves of such an electrode, but shows far greater brightness on the aluminium half. This probably depends, as has already been observed by Hittorf, on the fact that the resistance to passage is considerably greater on a silver kathode than on an aluminium one. If such an electrode, hitherto unused, having a perfectly fresh surface is used as the anode, the glow covers the whole of the anode side facing the kathode; and assuming that both halves are symmetrical with respect to the kathode, they show more or less approximately equal intensity. This extension of the glow is also maintained if the discharge is allowed to pass in the same direction, and occurs also if the passage of the current is broken and then re-established in the same direction. But if the current is reversed for a few seconds, so that the compound electrode acts as a kathode, and then the former direction is restored, the glow is bright on the silver half of the anode, but on the aluminium half it is either quite destitute of light, or so pale that special attention is necessary to see the light. The boundary of light exactly corresponds to the line of separation of the two surfaces. The discharge light at the anode accordingly despises that metal which is favoured by the kathode light, and occurs with brightness on that surface on which the kathode light shows the least intensity.

The phenomenon was also demonstrated also with a series of other electrode surfaces. In an aluminium circular disk of 4 centim. diameter, a star-shaped surface of silver was let in. The glow at the anode was limited to the silver star, the whole surrounding surface being destitute of light.

If in an aluminium disk, several centimetres in diameter, numerous detached silver points are inlaid in circles of $\frac{3}{4}$ millim. to $2\frac{1}{2}$ millim. in diameter, the anode luminosity occurs at all the silver points, while the intermediate aluminium parts remain dark. By arranging the silver points, any given luminous figures can be obtained, stars, arabesques, &c.

If, on the other hand, aluminium parts are let in a silver disk, the whole of the disk is luminous except the aluminium, which remains dark. If the anode consists of a chain of alternate links of aluminium and silver, only the silver ones are luminous. Silver when used as kathode in rarefied air soon tarnishes, becoming steel-yellow to steel-blue.

The author will elsewhere enter more minutely on the phenomenon described, especially as to the behaviour of other metals and in other gases.—*Verhandl. der Phys. Gesellschaft Berlin*, Dec. 16, 1892; Wiedemann's *Annalen*, May 1893.

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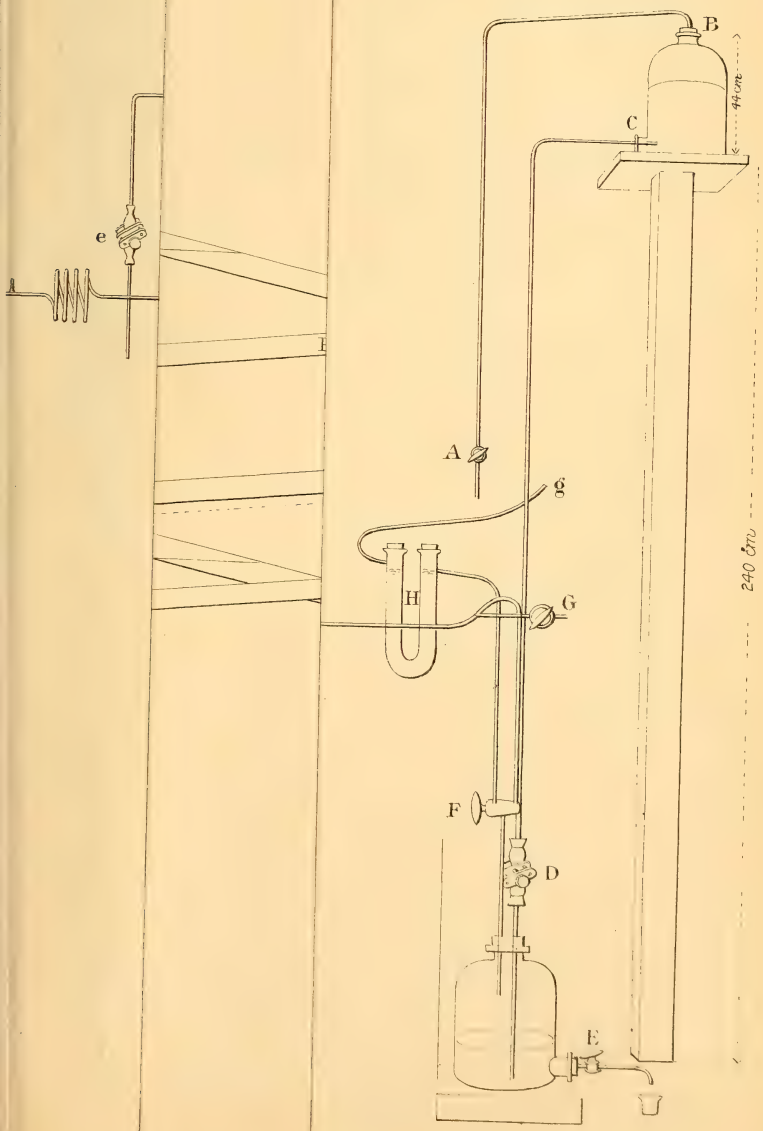

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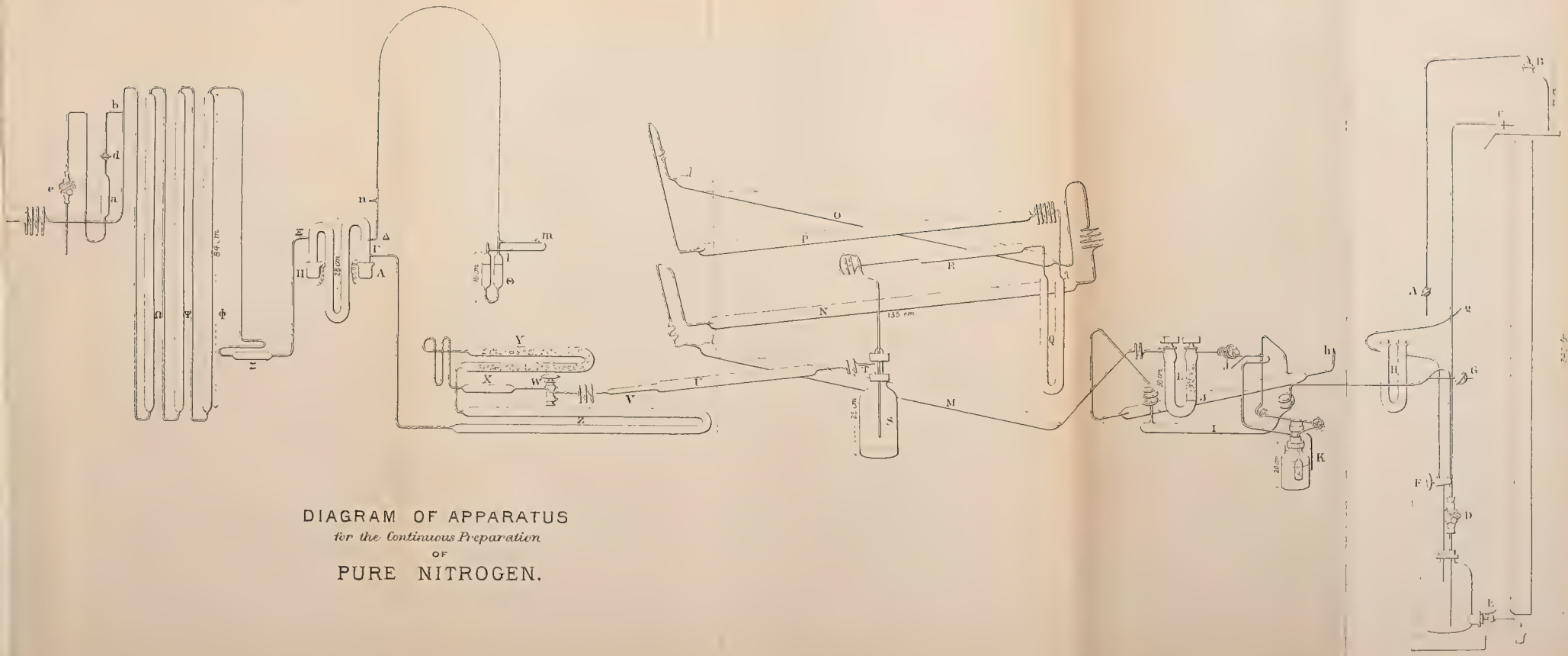

DIAGRAM OF APPARATUS
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OF
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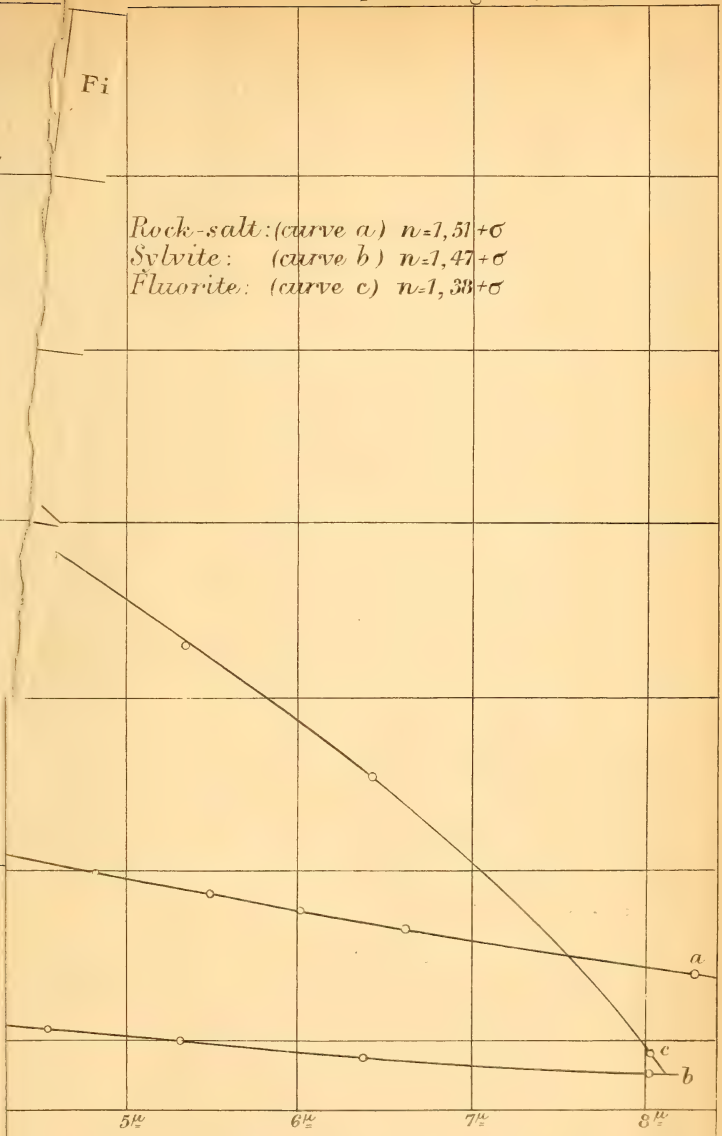

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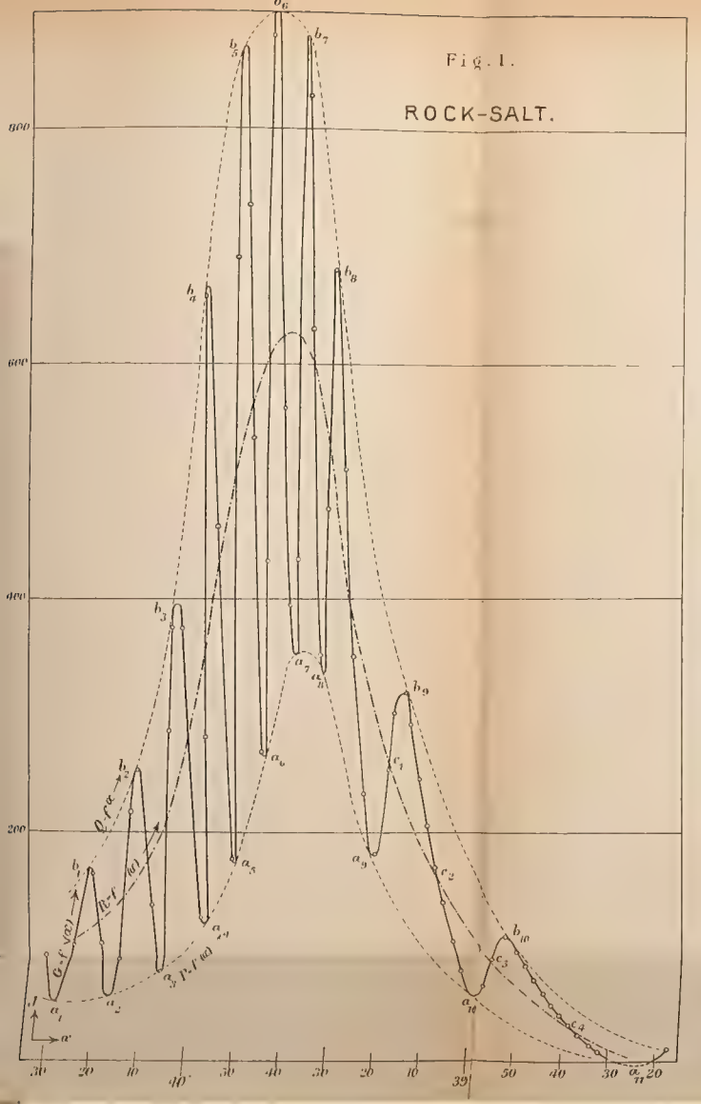

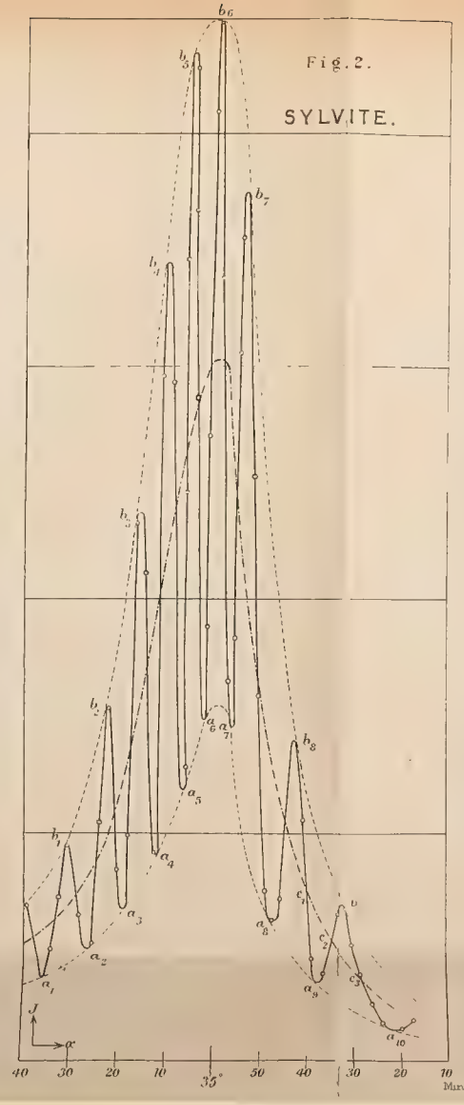

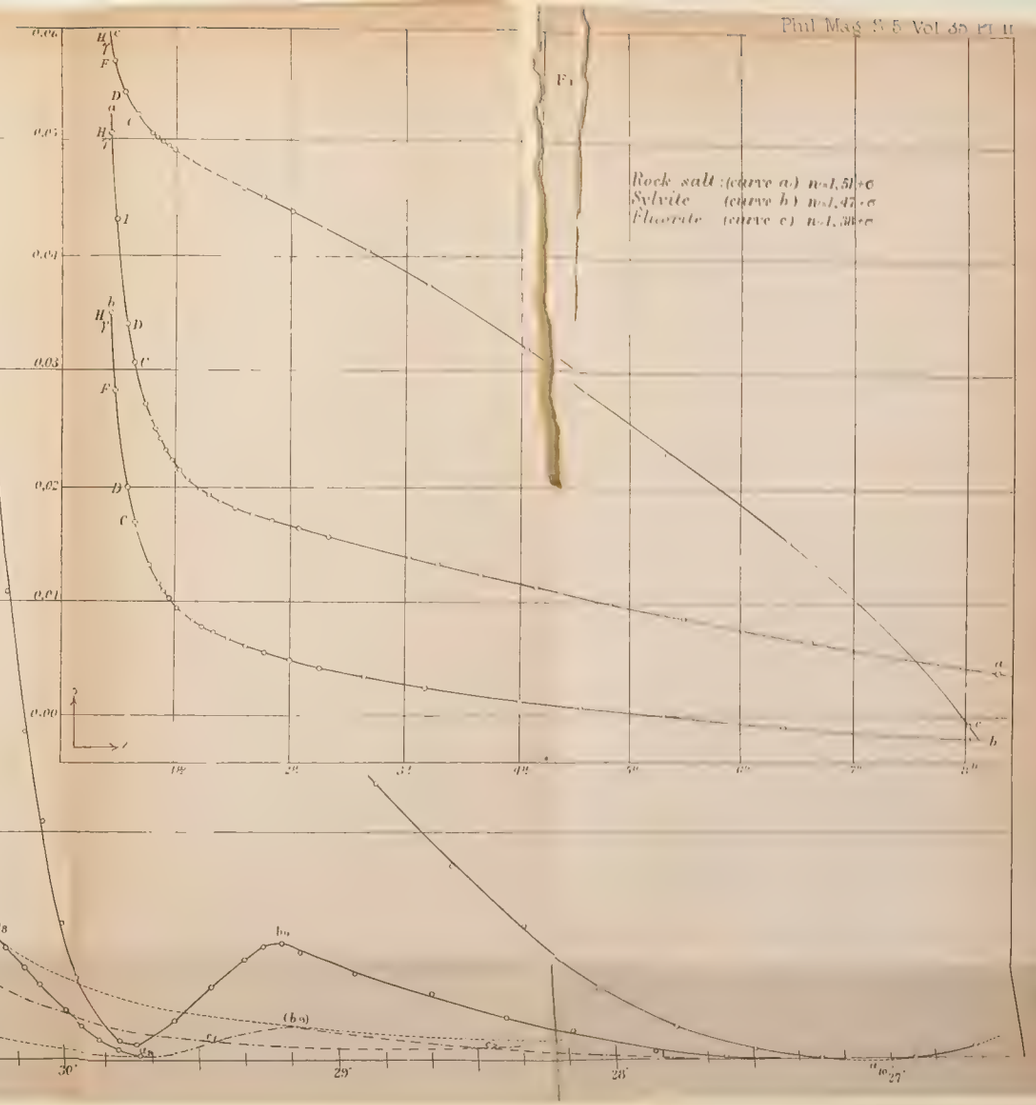

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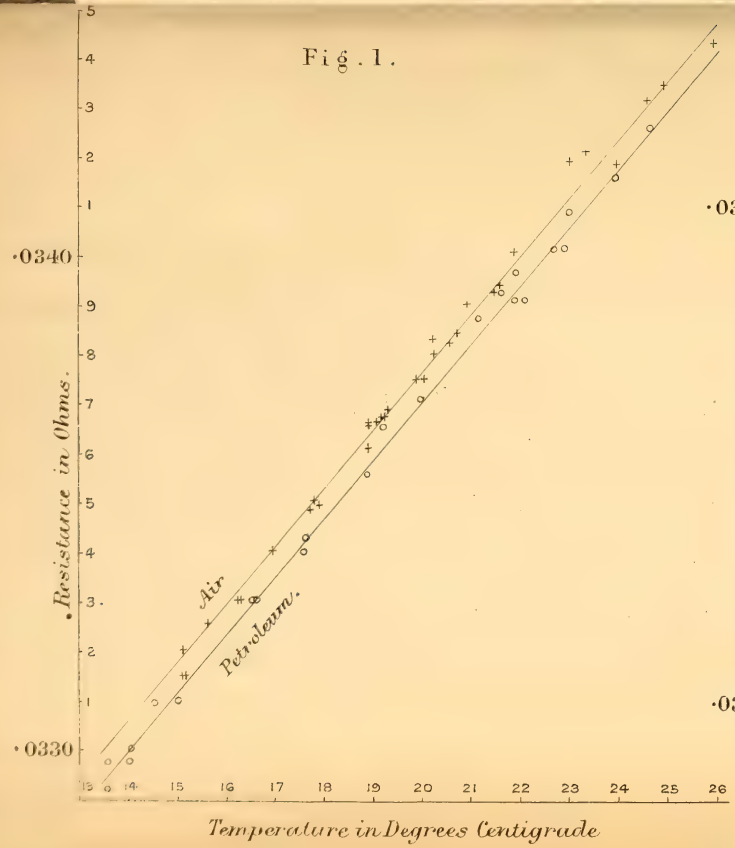

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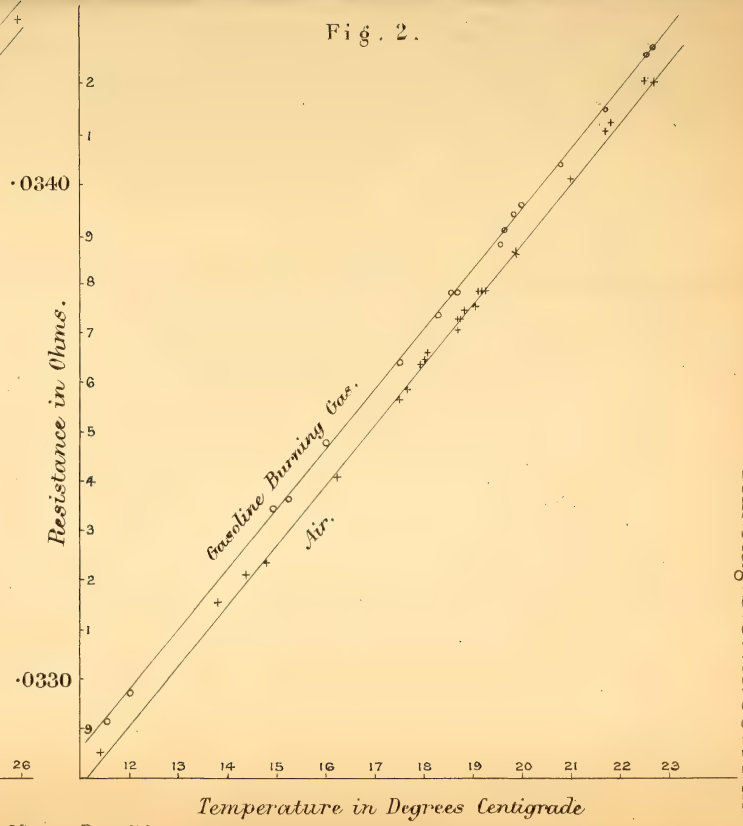

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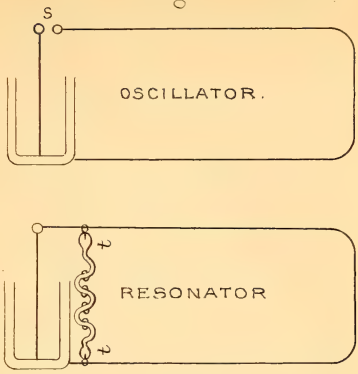

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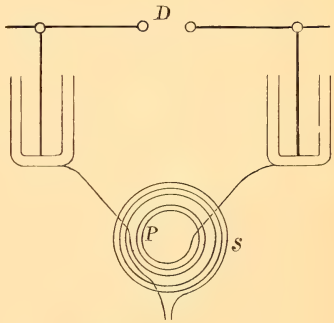

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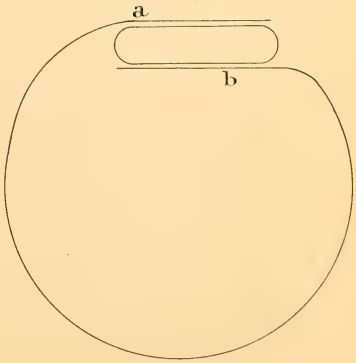

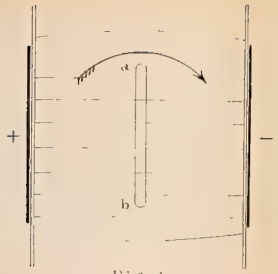

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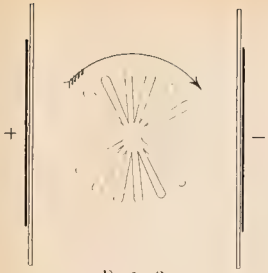

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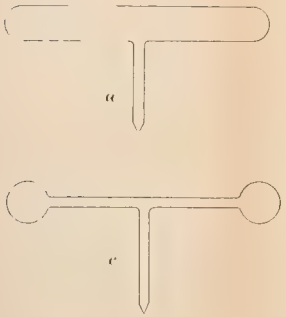

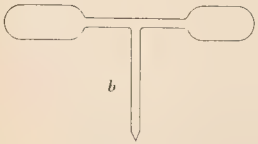

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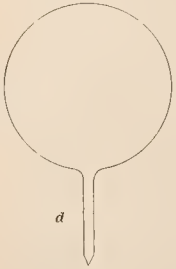

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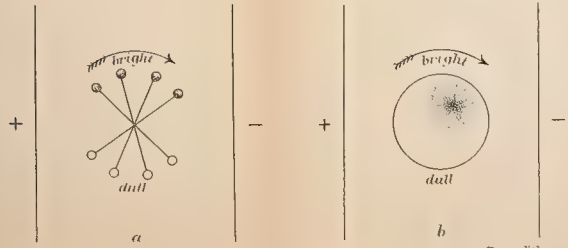

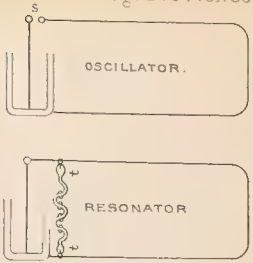

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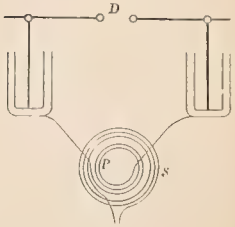

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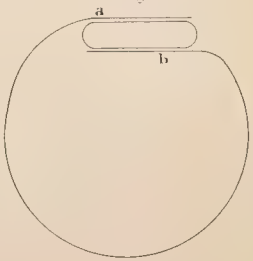

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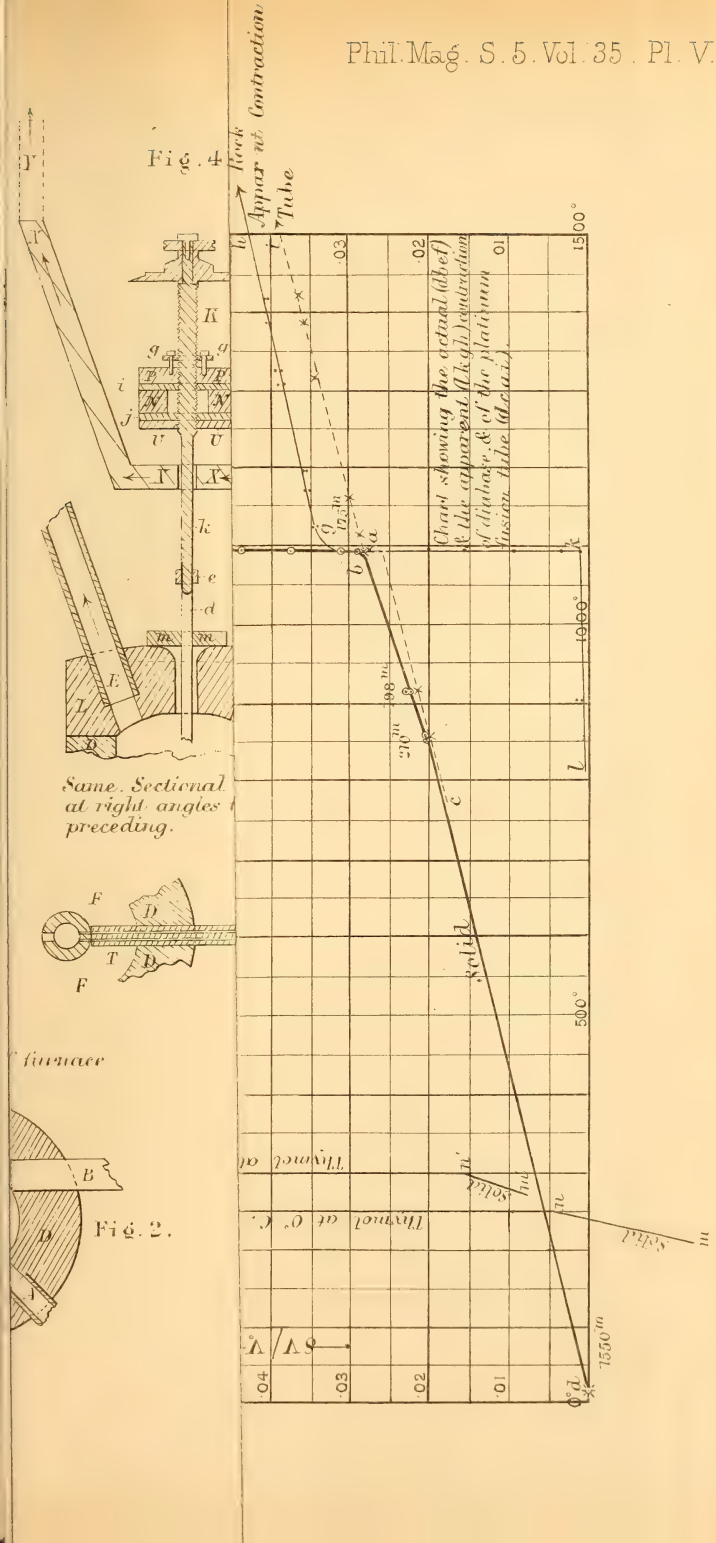
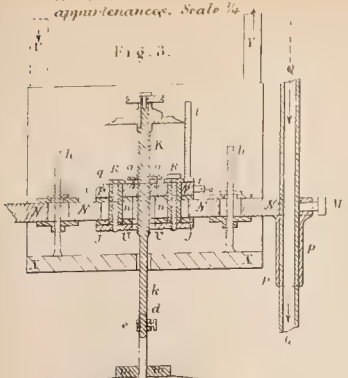


Fig. 4
Rock
Appar nt Contraction
Tube
Chart showing the actual (dbef) & the apparent (dkgh) contraction of diabase, & of the platinum fusion tube (dcai).
Same. Sectional at right angles preceding.
Solid
Thymol at
Thymol at 0° C.
Solid
Solid
1500°
1000°
500°
1550m
Fig. 2.

Vertical micrometer and appurtenances. Scale ¼

Fig. 3.



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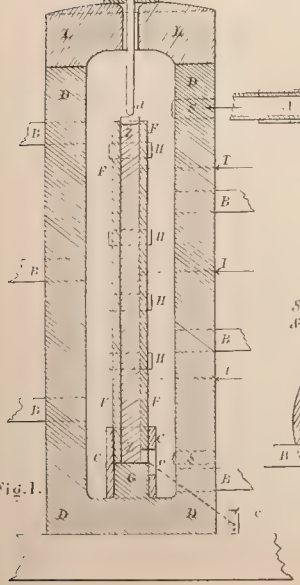


Sectional elevation of the furnace, showing the fusion tube, the sight tube, the burners, etc. Scale ¼.

Sectional plan of furnace & contents.

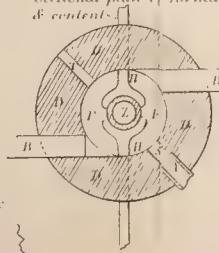
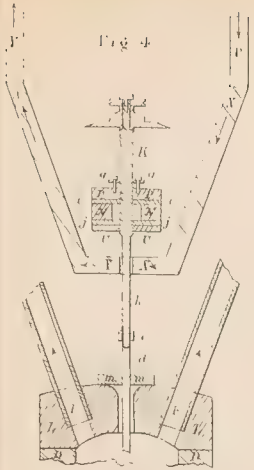


Fig. 2.

Fig. 4



Same. Sectional elevation at right angles to the preceding

Fig. 6

Clay envelope of the platinum fusion tube

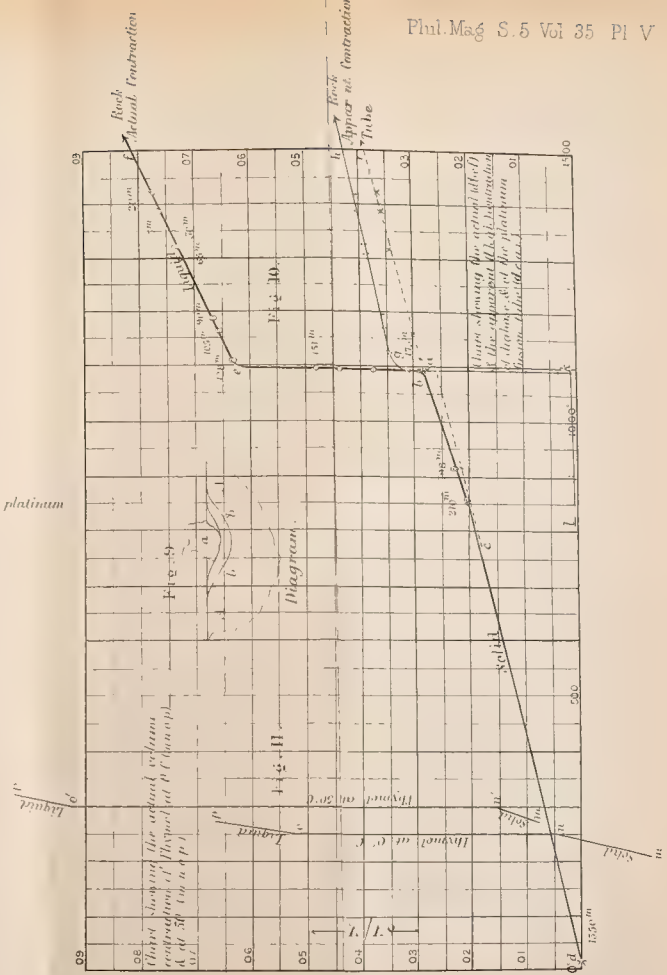
Fig. 8.
Method of adjusting the thermo couples

Fig. 7

Arm to hold the fusion tube

Fig. 5.

Perforated ring.



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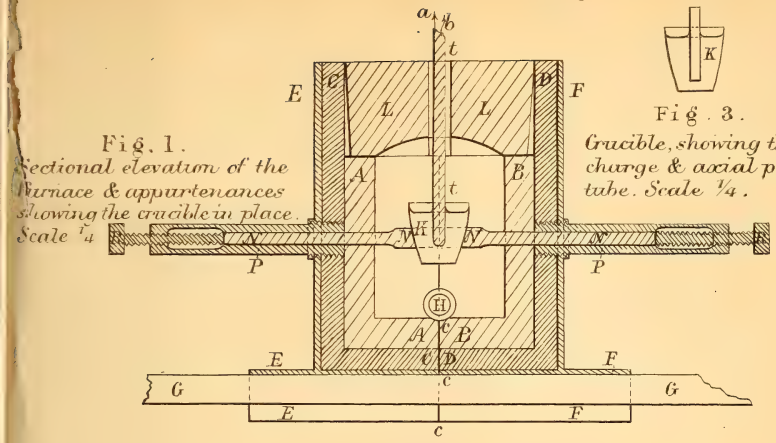

Fig. 1.
Sectional elevation of the furnace & appurtenances showing the crucible in place. Scale ¼

Fig. 3.
Crucible, showing the solid charge & axial platinum tube. Scale ¼.

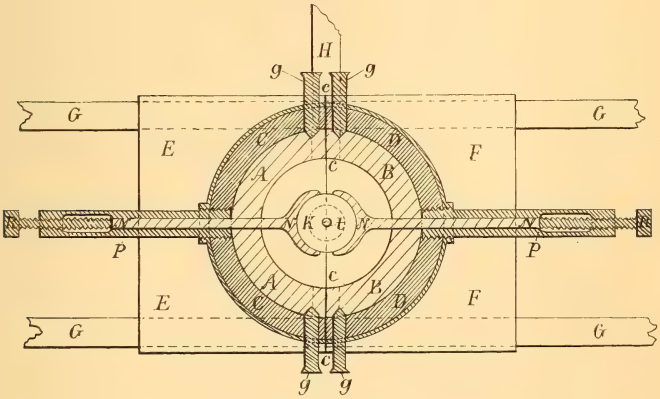

Fig. 2.
Sectional plan of furnace & crucible. Scale ¼.

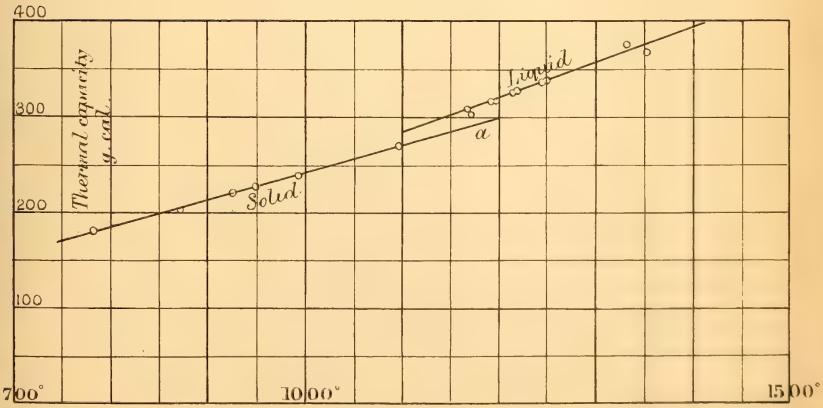

Fig. 4.
Chart, showing the relation of thermal capacity, solid & liquid, to temperature. Series II.

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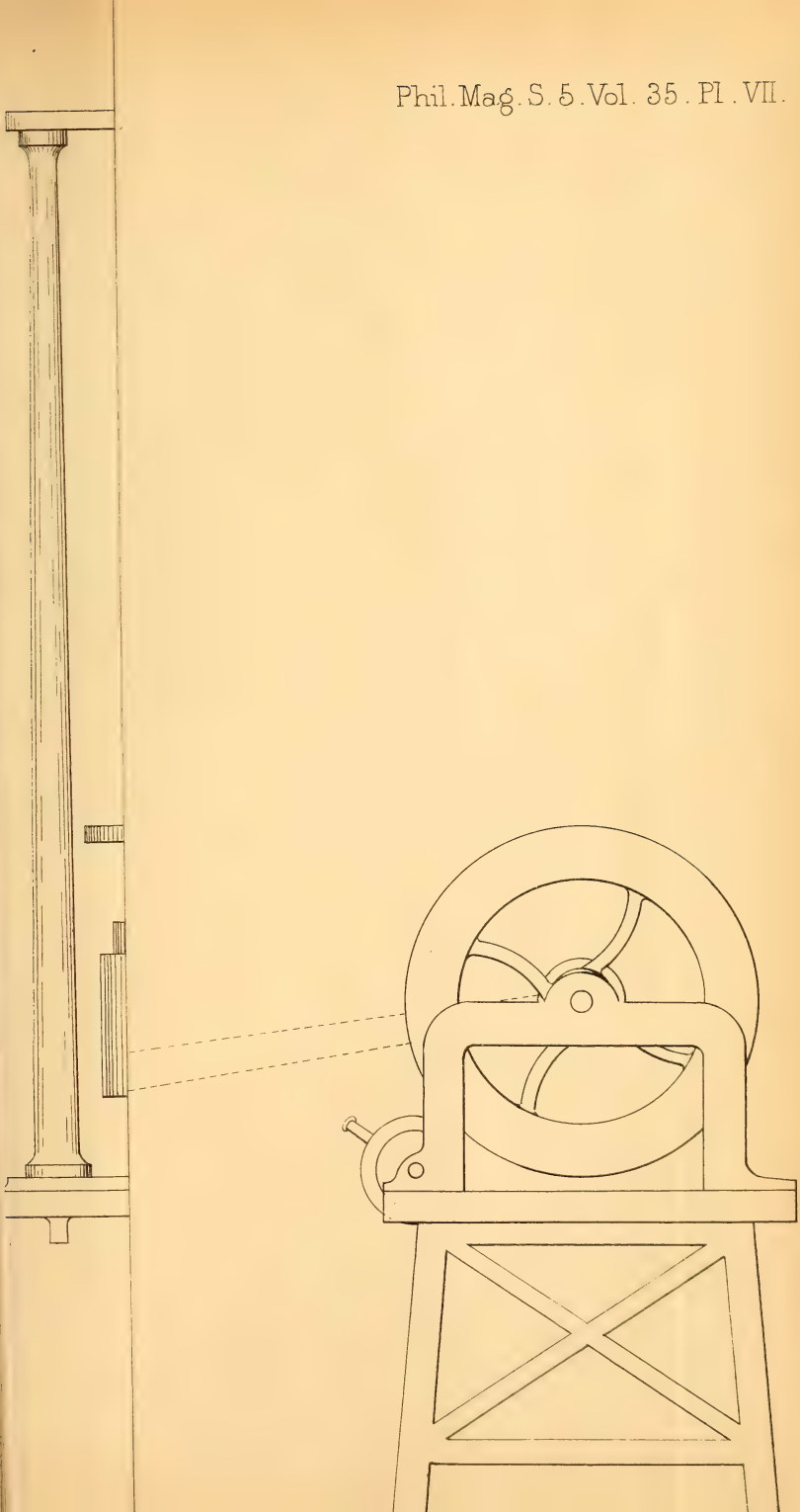


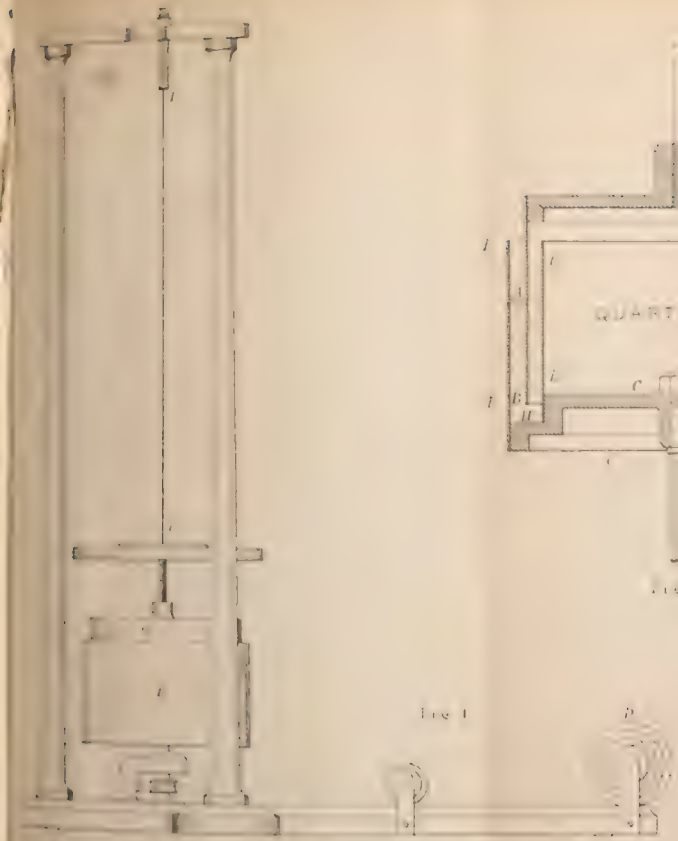
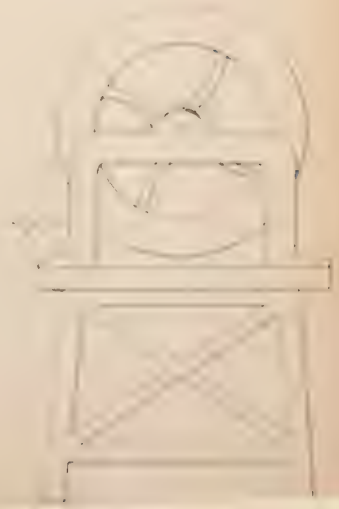


Fig. 1.

Fig. 2.



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